



Fast pyrolysis processes for biomass

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Abstract

Fast pyrolysis for production of liquids has developed considerably since the first experiments in the late 1970s. Many reactors and processes have been investigated and developed to the point where fast pyrolysis is now an accepted feasible and viable route to renewable liquid fuels, chemicals and derived products. It is also now clear that liquid products offer significant advantages in storage and transport over gas and heat. These advantages have caused greater attention to be paid to fast pyrolysis, leading to significant advances in process development.

The technology of fast pyrolysis for liquids is noteworthy for the wide range of reactor configurations that have been developed to meet the stringent requirements for high yields of useful liquids, for use as a fuel in boilers, engines and turbines and as a source of chemical commodities. This review summarises the key features of fast pyrolysis and the resultant liquid product and describes the major reaction systems and processes that have been developed over the last 20 years. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Renewable energy is of growing importance in satisfying environmental concerns over fossil fuel usage. Wood and other forms of biomass are one of the main renewable energy resources available. In contrast to other renewables, that give heat and power, biomass represents the only source of liquid, solid and gaseous fuels. Wood and other biomass can be treated in a number of different ways to provide such fuels. In general such methods are divided into biological (anaerobic digestion and fermentation) and thermal. As summarised in Fig. 1

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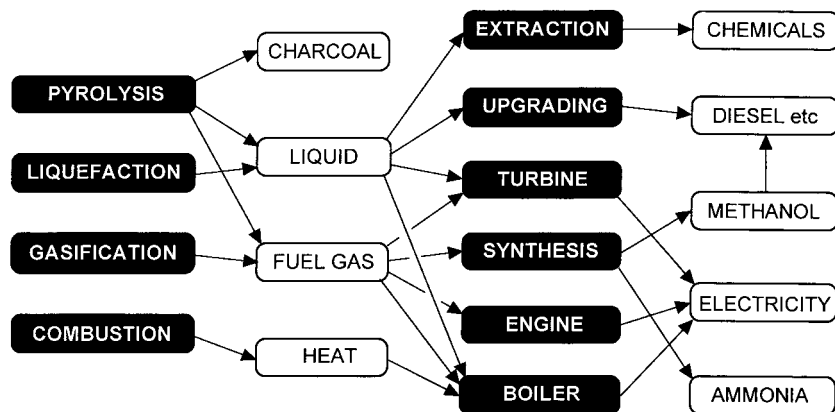
FAST PYROLYSIS PROCESSES FOR BIOMASS

Fig. 1. Thermochemical biomass processes and products.

thermal conversion processes include direct combustion to provide heat, for steam production and hence electricity generation. Gasification also provides a fuel gas that can be combusted, generating heat, or used in an engine or turbine for electricity generation. The third alternative is fast pyrolysis, that provides a liquid fuel that can substitute for fuel oil in any static heating or electricity generation application. The advantage of fast pyrolysis is that it can directly produce a liquid fuel, which is beneficial when biomass resources are remote from where the energy is required since the liquid can be readily stored and transported. Although slow pyrolysis is well known and an established process, for instance in charcoal production, fast pyrolysis is still under development. A review of direct thermal liquefaction was produced by Elliott et al. [1] and a survey of commercial and advanced technologies for both pyrolysis and gasification completed in 1994 [2].

1.1. Principles of fast pyrolysis

Fast pyrolysis is a high temperature process in which the feedstock is rapidly heated in the absence of air, vaporises and condenses to a dark brown mobile liquid which has a heating value of about half that of conventional fuel oil. While it is related to the traditional pyrolysis processes used for making charcoal, fast pyrolysis is a more advanced process that can be carefully controlled to give high yields of liquid.

The essential features of a fast pyrolysis process are:

- very high heating and heat transfer rates that requires a finely ground biomass feed;
- carefully controlled temperature of around 500°C;
- rapid cooling of the pyrolysis vapours to give the bio-oil product.

The main product, bio-oil, is obtained in yields of up to 80% wt on dry feed,

together with by-product char and gas which is used within the process so there are no waste streams.

1.2. Reactor configuration

While a wide range of reactor configurations have been operated, fluid beds and circulating fluid beds are the most popular configurations due to their ease of operation and ready scale-up.

1.3. Pyrolysis liquid–bio-oil

Fast pyrolysis liquids are dark brown and fluid, resembling a medium fuel oil in viscosity. The liquid is often referred to as ‘bio-oil’ or ‘bio-crude’ although it will not mix with any hydrocarbon liquids. Bio-oil is also sensitive to elevated temperatures when it undergoes chemical change so it cannot be distilled. They have a higher heating value of about 17 MJ/kg, as compared to around 42–44 MJ/kg for conventional fuel oil.

1.4. Applications for bio-oil

Bio-oil can substitute for fuel oil or diesel in many static applications including boilers, furnaces, engines and turbines. There are a range of chemicals that can be extracted or derived including food flavourings, specialities, resins, agri-chemicals, fertilisers, and emissions control agents. Upgrading bio-oil to transportation fuels is not economic, although technically feasible.

2. Fast pyrolysis system

A fast pyrolysis system consists of an integrated series of operations starting with a roughly prepared feedstock such as whole tree chips from short rotation coppice, energy crops such as miscanthus or sorghum, or agricultural residues such as straw. A conceptual fluidised bed fast pyrolysis system is shown in Fig. 2 indicating the main components that are discussed below.

2.1. Reception and storage

It is always necessary to provide for reception and handling and some storage of feed material. Low capacity systems of up to around 3 t/h feed can consist of a concrete pad for tipping delivered feed and a front end loader to move it between steps. As plants get larger, increasingly sophisticated reception, storage and handling systems will be required analogous to those employed in pulp and paper mills. This will include a weighbridge, tipping units, conveyors, bunker storage and reclamation.

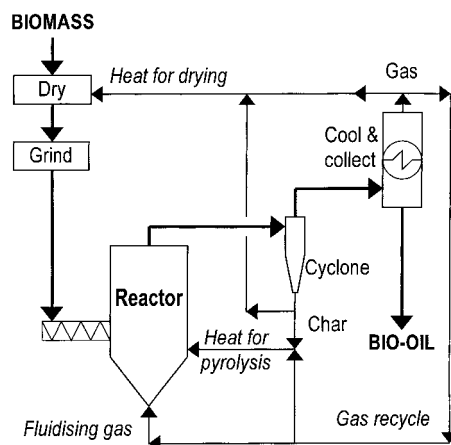


Fig. 2. Fast pyrolysis process principles.

2.2. Feed drying

Unless a naturally dry material such as straw is available, drying is usually essential as all the feed water is included in the liquid product. Low grade process heat would usually be employed, for example flue gases from by-product gas or char combustion using a rotary kiln. A detailed review of biomass drying has been prepared, see [157].

2.3. Grinding

Particles have to be very small to fulfil the requirements of rapid heating and to achieve high liquid yields. Feed specifications range from less than 200 μm for the rotating cone reactor to less than 2 mm for fluid beds and less than 6 mm for transported or circulating fluid beds. Ablative reactors can utilise whole tree chips as the mechanism of heat transfer is different. Size reduction becomes increasingly expensive as size reduces and reactors using larger particles have an advantage in this respect.

2.4. Reactor configuration

A wide range of reactor configurations have been investigated (see Table 1) that show considerable diversity and innovation in meeting the basic requirements of fast pyrolysis. The 'best' method is not yet established with most processes giving between 65–75% liquids based on dry wood input.

The essential features of a fast pyrolysis reactor are: very high heating and heat transfer rates; moderate and carefully controlled temperature; and rapid cooling

Table 1
Fast pyrolysis reactor types and locations

Reactor type	Organisations
Fluid bed	Aston University, Dynamotive, Hamburg University, INETI, IWC, Leeds University, NREL, Oldenberg University, RTI, Sassari University, UEF, VTT, Zaragoza University, ZSW-Stuttgart University
Ablative	NREL, Aston University, BBC, Castle Capital
Circulating fluid bed	CRES, CPERI, ENEL/Pasquali
Entrained flow	GTRI, Egemin
Rotating cone	Twente University, BTG/Schelde/Kara
Transported bed	Ensyn, (at ENEL, Red Arrow, VTT)
Vacuum moving bed	Laval University/Pyrovac

or quenching of the pyrolysis vapours [3,4]. Commercial operation is currently only being achieved from a transport or circulation fluid bed system that are used to produce food flavourings. Fluid beds have also been extensively researched and are an ideal R&D tool and have been scaled up to pilot plant size with plans in hand for demonstration in several locations. Substantial developments can be expected in performance and cost reduction in coming years.

2.5. Char and ash separation

Some fine char is inevitably carried over from cyclones. Unless removed by a hot vapour filter, which is still under development, it will collect in the liquid and can only be removed by liquid filtration using for example cartridge or rotary filters. Almost all of the ash in the biomass is retained in the char, so successful char removal gives successful ash removal. Char separation, however, is difficult and may not be necessary for all applications.

Char contributes to secondary cracking by catalysing secondary cracking in the vapour phase. Rapid and complete char separation is therefore desirable. Even char in the cooled collected liquid product contributes to the instability problems, accelerating the slow polymerisation processes which manifest as increasing viscosity.

2.6. Vapour residence time

The time and temperature profile between formation of pyrolysis vapours and their quenching influences the composition and quality of the liquid product. High temperatures will continue to crack the vapours and the longer the vapours are at higher temperatures, the greater the extent of cracking. Although secondary reactions become slow below around 350°C, some secondary reactions will continue down to room temperature which contributes to the instability of the

bio-oil. The time-temperature envelope that the pyrolysis vapours endure will affect the oil quality. Char also contributes to vapour cracking as described above. Vapour residence times of a few hundred milliseconds are necessary for optimum yields of chemicals and food additives, while fuels can tolerate vapour residence times of up to around 2 s. Longer residence times result in significant reductions in organic yields from cracking reactions.

2.7. Liquid collection

The collection of liquids has long been a major difficulty in the operation of fast pyrolysis processes due to the nature of the liquid product which is mostly in the form of aerosols rather than a true vapour. Quenching, i.e. contact with cooled liquid is effective but careful design and temperature control is needed to avoid blockage from differential condensation of heavy ends. Light ends collection is important in reducing liquid viscosity. Electrostatic precipitation has been shown to be very effective in recovering the aerosols. In fluid bed type systems the vapour/aerosol concentration can be very low, further increasing the difficulty of product separation due to the low vapour pressure.

2.8. Fast pyrolysis design considerations

The above considerations are summarised in Table 2 with key features identified and defined.

Table 2
Key fast pyrolysis design features

Pretreatment	
Feed drying	Essential to ~10%
Particle size	Small particles needed. Costly
Washing and additives	For chemicals production
Reactor	
Reactor configuration	Many configurations have been developed, but there is no best one
Heat supply	High heat transfer rate needed
Heat transfer	Gas-solid and/or solid-solid
Heating rates	Wood conductivity limits heating rate
Reaction temperature	500°C maximises liquids from wood
Product conditioning and collection	
Vapour residence time	Critical for chemicals, less for fuels
Secondary cracking	Reduces yields
Char separation	Difficult from vapour or liquid
Ash separation	More difficult than char separation
Liquids collection	Difficult. Quench and EP seem best

3. Current status

Europe has only relatively recently become involved in direct production of liquid fuels from biomass. Up to 1989, the only European plant was a conventional (slow) pyrolysis demonstration plant of 500 kg/h operating in Italy for liquid and char production with approximately 25% yield of each [5]. This was the Alten plant and is described below. Around the same time, Bio-Alternative in Switzerland was operating a fixed bed carbonisation pilot plant fed with wood, waste and MSW for charcoal production with secondary liquids as a low yielding by-product at up to 20 wt% yield [6]. Tests were carried out on combustion of these oils [7]. Both these activities served to foster interest in direct production of liquids from biomass in atmospheric processes as well as creating concerns over poor liquid quality and low yields that still linger.

Subsequently, a 200 kg/h fast pyrolysis pilot plant based on the University of Waterloo (Canada) process was constructed in Spain by Union Fenosa which started up in mid 1993 [8,9]. Egemin in Belgium built and operated a 200 kg/h capacity entrained downflow pilot plant to their own design which started up in July 1991 and operated until late 1992 [10]. ENEL purchased a 15 t/d Ensyn RTP3 pilot plant to produce bio-oils for testing which was installed at Bastardo in Italy in mid 1996 [11]. All these processes are described in more detail below with other exploratory studies sponsored by the EC JOULE and FAIR programmes. These are listed in Table 3. The inclusion of fast pyrolysis in the 4th Non Fossil Fuel Obligation (NFFO) tranche in the UK in 1996 served to heighten awareness of the technology and caused a considerable increase in interest in Europe.

In North America a number of commercial and demonstration plants for fast pyrolysis have been operating in North America at a scale of up to 2000 kg/h. Ensyn (Canada) are marketing commercial fast pyrolysis plants of up to 10 t/h throughput which are offered with a performance guarantee and a number of conditional sales have been concluded [12]. Two plants of around 1 t/h capacity are operated regularly in the USA for food flavourings production which is still the only commercial application for fast pyrolysis [13]. Castle Capital have acquired the Continuous Ablative Reaction (CAR) process developed by BBC and until 1996 were operating a 1–2 t/h plant near Halifax, Nova Scotia, Canada [14]. The second generation 1360 kg/h Interchem demonstration plant in Kansas based on the NREL vortex ablative pyrolysis process [15] has been finally abandoned.

4. Pyrolysis processes

The significant research, demonstration and commercial processes that are based on pyrolysis for production of liquids are listed in Table 3, arranged in size order. Dormant or dismantled or abandoned processes are only included if there is useful information available. Both fast and slow pyrolysis processes are included in Table 4 as slow pyrolysis processes for liquids contain some technical parallels and the expertise and related support is closely related to fast pyrolysis.

Table 3
Pyrolysis liquids production processes, 1998

Host organisation	Country	Technology	kg/h	Status
Castle Capital ^a	Canada	Ablative tube ^a	2000	Shut down
Dynamotive	Canada	Fluid bed	1500	Design
Interchem	USA	Ablative vortex	1360	Abandoned 1994
Red Arrow/Ensyn	USA	Circulating transported bed	1250	Operational
Red Arrow/Ensyn	USA	Circulating transported bed	1000	Operational
ENEL/Ensyn	Italy	Circulating transported bed	625	Operational
Alten	Italy	Stirred/fluid bed	500	Abandoned 1992
BTG/Kara	Netherlands	Rotating cone	200	Design
Union Fenosa/Waterloo	Spain	Fluid bed	200	Operational
Egemin	Belgium	Entrained flow	200	Abandoned 1992
Red Arrow/Ensyn	Canada	Circulating transported bed	125	Operational
Ensyn	Canada	Circulating transported bed	100	Operational
Pasquali/ENEL	Italy	Circulating fluid bed (CIRO)	50	Shut down
GTRI	USA	Entrained flow	50	Abandoned 1990
BBC	Canada	Ablative tube	50	Shut down
Bio-Alternative ^b	Switzerland	Fixed bed ^b	50	Abandoned 1993
BTG	Netherlands	Rotating cone	50	Operational
University of Hamburg	Germany	Fluid bed	50	Operational
University of Laval	Canada	Vacuum moving bed	50	Operational
University of Shenyang	China	Rotating cone	50	Shut down
WWTC ^b	Canada	Augur kiln ^b	42	Operational
Ensyn	Canada	Circulating transported bed	40	Operational
Dynamotive	Canada	Fluid bed	20	Operational
NREL	USA	Ablative vortex	30	Dismantled 1997
NREL	USA	Ablative vortex	20	Operational ^a
RTI	Canada	Fluid bed	20	Operational
VTT/Ensyn	Finland	Circulating transported bed	20	Operational
CRES	Greece	Circulating fluid bed	10	Operational
Ensyn	Canada	Circulating transported bed	10	Operational
University of Tübingen ^b	Germany	Augur kiln ^b	10	Operational
University of Twente	Netherlands	Rotating cone	10	Operational
BFH/IWC	Germany	Fluid bed	6	Operational
INETI	Portugal	Fluid bed	5	Operational
University of Aston	UK	Ablative plate	5	Operational
RTI	Canada	Fluid bed	3	Dismantled
University of Aston	UK	Ablative plate	3	Operational
University of Waterloo	Canada	Fluid bed	3	Moved to RTI 1995
University of Aston	UK	Fluid bed	2	Operational
CPERI	Greece	Circulating fluid bed	1	Re-building
BFH (IWC)	Germany	Fluid bed	< 1	Operational
Colorado School Mines	USA	Ablative mill	< 1	Dismantled 1990
CPERI	Greece	Fluid bed	< 1	Dismantled
NREL	USA	Fluid bed	< 1	Operational
RTI	Canada	Fluid bed	< 1	Operational
University of Aston	UK	Fluid bed	< 1	Operational
University of Leeds	UK	Fluid bed	< 1	Operational
University of Oldenburg	Germany	Fluid bed	< 1	Operational

Table 3 (continued)

Host organisation	Country	Technology	kg/h	Status
University of Technology	Malaysia	Fluid bed	< 1	Operational
University of Santiago	Spain	Fluid bed	< 1	Design
University of Sassari	Italy	Fluid bed	< 1	Operational
University of Stuttgart (ZSW)	Germany	Fluid bed	< 1	Shut down
University of Zaragoza	Spain	Fluid bed	< 1	Operational
VTT	Finland	Fluid bed	< 1	Operational

^a Operated as a gasifier with all gas and vapours combusted, but can produce liquids.

^b Slow pyrolysis for liquids production.

4.1. Alten, Italy

4.1.1. Introduction

Alten stands for Alternative Energy Technologies which was a consortium of KTI and Italenergie, but is no longer in partnership. The aim of this activity was to develop a small scale pyrolysis process to convert wood and agricultural wastes into marketable fuel products such as fuel oil, charcoal and char-water slurries. It was envisaged that a network of small pyrolysis plants would produce bio-oil to fire a 27 MWe power station in Avezzano. The pyrolysis plant was in operation from 1985 to 1990, and was the largest pyrolysis plant for liquids plant built in Europe until 1996. It provided valuable data on process design, optimisation, and qualitative results as well as substantial quantities of oil for testing.

The design capacity of the plant was 1 t/h dry biomass, but only up to 500 kg/h were achieved on a continuous basis [16]. The nature of the process was that relatively slow pyrolysis occurred in the stirred or fluid bed reactor giving a secondary oil that had a low water tolerance and high viscosity. Although the product quality caused problems, the availability of large quantities of pyrolysis liquids for testing and evaluation caused serious attention to be focused on direct liquefaction for the first time in Europe.

4.1.2. Description

Fig. 3 is a flowsheet of the process [16,17]. Feedstocks tested included wood chips, olive husks, straw and vine trimmings. The feed was screened, re-chipped and dried in a rotary drier before entering the fluid bed reactor. The drying fuel was propane, but the product fuel gas would be used in a commercial venture. Air was added to the reactor to give a partial gasification reaction to provide reaction heat. This results in a poor quality, low heating value fuel gas. Another new feature was the provision of reaction heat for pyrolysis by partial oxidation in a fluid bed, although this principle has always been used for classical carbonisation in batch units.

The reaction temperature and pressure are about 500°C and 1 atm respectively. The char formed is separated from the vapour stream in a hot gas cyclone. The char is cooled in a sequence of water cooled screw conveyors and stored in a silo.

Table 4

Organisations with pyrolysis processes for liquids. (Those in **bold** are described in the text that follows with key references)

Organisation	Country	Technology	Status	
Alten^a	Italy	Own	Fluid or stirred bed	Dismantled
BBC	Canada	Own	Ablative tube	Operational
BFH (IWC)	Germany	Own	Fluid beds	Operational
Bio-Alternative^a	Switzerland	Own	Fixed bed	Shut down
BTG	Netherlands	Twente	Rotating cone	Operational
Castle Capital	Canada	BBC	Ablative tube	Dismantled, <i>see BBC</i>
Colorado School of Mines	USA	Own	Ablative mill	Dismantled
CPERI	Greece	Own	Circulating fluid bed	Re-build
CRES	Greece	Own	Circulating fluid bed	Operational
Dynamotive	Canada	RTI	Fluid bed	Operation
<i>Ecotechniek</i>	<i>Netherlands</i>			<i>see Pyrovac</i>
Egemin	Belgium	Own	Entrained flow	Shut down
<i>ENEL</i>	<i>Italy</i>			<i>see Pasquali</i>
<i>ENEL</i>	<i>Italy</i>			<i>see Ensyn</i>
Ensyn	Canada	Own	Transported bed	Operational
GTRI	USA	Own	Entrained flow	Dormant
INETI	Portugal	Own	Fluid bed	Operational
Interchem	USA	NREL	Ablative vortex	Abandoned
NREL	USA	Own	Ablative vortex	Operational
NREL	USA	Own	Fluid bed	Operational
Pasquali/ENEL	Italy	Own	Circulating fluid bed	Operational
Pyrovac	Canada	Own	Vacuum moving bed	Operational
<i>Red Arrow</i>	<i>USA</i>			<i>see Ensyn</i>
RTI	Canada	Own	Fluid bed	Operational
Stenau	Germany	Tübingen	Rotary kiln	Operational
TWT	Canada	Own	Stirred/fluid bed	Shut down
	Spain	Waterloo	Fluid bed	Operational
University of Aston	UK	Own	Ablative	Operational
University of Aston	UK	RTI	Fluid bed	Operational
<i>University of Athens, Agricultural</i>	<i>Greece</i>	<i>Own</i>	<i>Circulating fluid bed</i>	<i>see CRES</i>
<i>University of Laval</i>	<i>Canada</i>	<i>Own</i>	<i>Vacuum moving bed</i>	<i>See Pyrovac</i>
University of Leeds	UK	Own	Fluid bed	Operational
University London Imperial College	UK	Own	Heated grid	Dormant
University of Santiago	Spain	RTI	Fluid bed	Design
University of Sassari	Italy	Own	Fluid bed	Dormant
University of Stuttgart	Germany	RTI	Fluid bed	Shut down
University of Tübingen^a	Germany	Own	Auger kiln	Operational
University of Twente	Netherlands	Own	Rotating cone	Operational
University of Waterloo	Canada	Own	Fluid bed	Moved to RTI 1995
<i>VTT</i>	<i>Finland</i>	<i>Ensyn</i>		<i>see Ensyn</i>
VTT	Finland	Waterloo	Fluid bed	Operational

^a Slow pyrolysis for liquids.

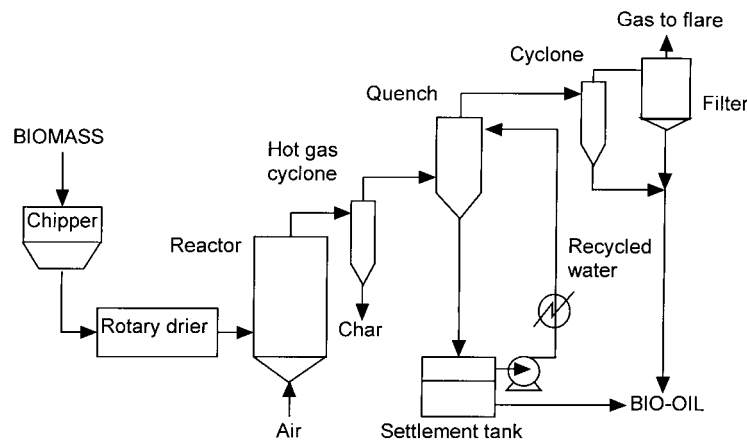


Fig. 3. Alten flow diagram.

The reactor was not well defined—it was specified as a fluid bed, but seemed to behave more like a stirred bed. As the primary objective was the production of oil for testing, little instrumentation was available.

The vapour and gas streams passed through a countercurrent quench vessel where they were cooled and condensed by countercurrent direct contact with recycled product water. The mixture of oil and water was separated in a settlement tank before sending the oil to storage and recycling the water through an air cooler. Excess water was removed to maintain a constant height interface in the settlement tank. The resulting water condensate had a very high COD at around 150,000 and would require extensive treatment before disposal or discharge. Further liquid was removed from the product gas firstly in a cyclone then a demister/filter, before burning the gas in a flare. The gas from the drier was also sent to the flare to eliminate pollutants. The gas could potentially be used internally as a fuel source for drying the feed or other process heat applications. A typical mass balance and energy output is shown in Table 5.

4.1.3. Products

The pyrolysis liquid was black and viscous and sometimes contained a

Table 5
Alten typical mass balance (Basis: 100 kg d.a.f. biomass feed)

Inputs	kg	Outputs	kg	HHV, MJ/kg	%Energy
Dry biomass	100.0	Charcoal	20.5	29.7	32
Moisture	2.0	Bio-oil	20.5	26.3	28
Pyrolysis air	39.0	Fuel gas	100.0	4.1	32
		Losses	—		8
Total	141.0	Total	141.0		100

significant proportion of charcoal of up to 15% by weight of the oil. This caused a ‘lumpy’ texture in early samples. A typical pyrolysis liquid analysis and a gas analysis is given in Table 6. The char was a coarse powder with particle sizes ranging from 40–50 μm to several mm, similar to the size and shape characteristics of the feed.

4.2. BBC, Canada

4.2.1. Introduction

This work was instigated to assess fast pyrolysis as an alternative method for tyre disposal. The primary objective was to demonstrate that short residence times and high heating rates could produce high yields of liquids from rubber. A 10–25 kg/h unit was constructed to investigate the reactor parameters of surface temperature and gas/vapour product residence time and particle size. The system is expected to be capable of using wood as a feedstock.

Table 6
Alten process—typical product analysis

Liquid	
Elemental analysis (wet basis)	
C (% wt)	61.90
H (% wt)	6.00
N (% wt)	1.05
S (% wt)	0.03
O (% wt, by difference)	31.02
H/C ratio	1.16
O/C ratio	0.18
Moisture (% wt)	14.60
Ash (% wt)	1.50
Char content (% wt)	9.20
Viscosity, cp@70°C	55
HHV, MJ/kg	26.3
Specific gravity (15/4°C)	1.195
Gas	
CO	27.6% vol
CO ₂	21.8% vol
H ₂	4.7% vol
O ₂	0.7% vol
N ₂	38.2% vol
CH ₄	4.7% vol
C ₂ H ₄	0.4% vol
C ₂ H ₆	0.3% vol
Others (by difference)	1.6% vol
Higher heating value	5 MJ/Nm ³
Solid	
Volatiles	15–20%
Higher heating value	29.5 MJ/kg
Empirical formula	CH _{0.25} O _{0.07}

The process technology has been sold or licensed to Castle Capital who have installed a 1500–2000 kg/h plant in Halifax, Nova Scotia, using solid waste as feed. This is described later. This operates at higher temperatures giving a gas product but can be modified to produce liquids.

4.2.2. Description

Limited details of the continuous ablation reactor (C.A.R.) are available from patent applications [18]. Ablation is achieved by sliding contact of the rubber particles on a hot metal surface. Tests on a 50 kg/h pilot reactor have demonstrated efficient heat and mass transfer and a smaller test unit is presently operating at a throughput of 10–25 kg/h. Particles up to 6 mm have been used with liquid recovery in a two stage direct liquid quench of the product vapours with recycled liquids after char removal in a high temperature cyclone. The system is shown in Fig. 4.

Tyre rubber is used with a particle size of 1–3 mm. The feeder is mounted on load cells and comprises a pressurised lock hopper with a variable speed discharge screw which feeds the reactor. The reactor has staged external heating for zonal temperature control and catalysts can be added to the reactor. Vapour product residence time in the reactor is controlled by the addition of nitrogen and is separated from the char and metal in a cyclone before quenching in a baffle plate column. Liquids are then collected in a sump tank and are returned to the column via a water cooled heat exchanger, with a proportion being pumped to storage. The first column is operated at 100°C exit temperature of the vapour/gas

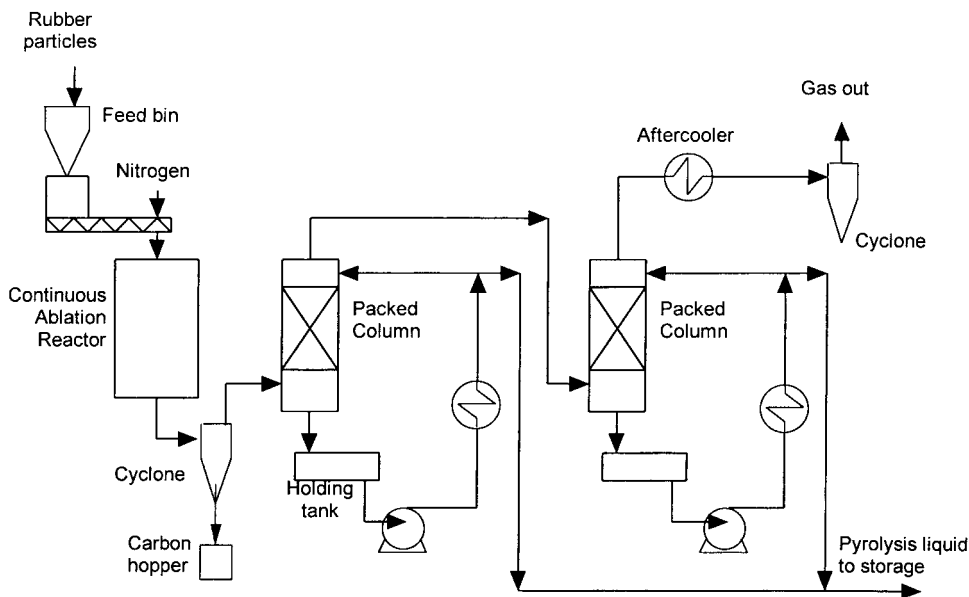


Fig. 4. BBC continuous ablation reactor system.

products. The second column is similar to the first with a final gas exit temperature of 40°C.

Problems have occurred during sustained periods of operation where the fine carbon black ($< 3 \mu\text{m}$) gradually made the recycled liquid in the first collection column too viscous to pump after 2 h. Approximately 30% of the char formed was too fine to be efficiently recovered by the cyclone. A particle size analysis of the product char showed it all to be less than $10 \mu\text{m}$. Modification of the system, which has not been detailed, allowed operation to be extended to 3 h. Black suggests that liquid filtration will solve the problem, which may prove difficult in view of the particle size of less than $10 \mu\text{m}$.

4.2.3. Products

Liquid yields of 54% have been obtained from tyres at 470–540°C at 0.88 s residence time and 1.3 mm size particles. Liquid composition and mass balances are given in Table 7 [19]. There are no results available for biomass feedstocks.

Table 7
Some results for the BBC continuous ablation reactor from tyres

Tyres feed (wt% of liquid)	run: Apr 2b
Feed ash content (wt%)	7.1
Reactor temperature (°C)	450
Residence time (s)	0.925
Char	52.9
Liquid	39.1
Benzene	0.135
Styrene	1.3
Toluene	0.95
Limonene	0.35
Ethylbenzene	0.24
Naphthalene	0.15
Xylenes	1.12
Total aromatics	26
Gas (inert free)	8.0
Composition (N ₂ free basis)	
H ₂	0.22
CO ₂	5.25
CO	0.00
CH ₄	9.96
C ₂ H ₄	16.26
C ₂ H ₆	4.60
C ₃ H ₆	11.49
C ₃ H ₈	1.63
1-butene	26.52
butadiene	15.37
other C ₄ 's	5.69
C ₅ +	3.00

4.3. BFH (Institute for Wood Chemistry), Germany

4.3.1. Introduction

BFH stands for Bundesforschungsanstalt für Forst- und Holzwirtschaft (Federal Research Centre for Forestry and Forest Products) and comprises eight institutes, of which one is the Institute for Wood Chemistry and Chemical Technology of Wood (IWC).

IWC has different departments and in the lignin department thermochemical conversion of biomass and lignin have been studied since the 1970s at different scales and with different objectives. Since 1984 analytical pyrolysis in combination with GC/MS has become one of the principal methods at IWC for the characterization of lignocellulosic feedstocks. A huge mass spectral library has been built up for the identification of degradation products.

From 1982 to 1994 high pressure conversion technology was used to directly liquefy biomass and technical lignins in the presence of a catalyst at high hydrogen pressures. Under certain reaction conditions no char was formed and liquid yields were in the range of 65–75%.

Since 1993 fast pyrolysis in fluidized bed reactors has been investigated in a laboratory scale (100–200 g/h) and pilot scale unit (5 kg/h). Start-up of the laboratory scale reactor was in 1993 and for the pilot plant in 1997. Deutsche Bundesstiftung Umwelt (German Foundation for Environment) funded a project from 1995–1997 for the fluid bed fast pyrolysis of contaminated wood wastes at laboratory and pilot plant scale unit. Fresh and contaminated wood has been studied in order to devise a better disposal method for such wastes combined with energy recovery. Germany's new regulations for waste treatment, incineration and landfill have become so restrictive that pyrolysis seems to be an attractive alternative.

4.3.2. Bench scale unit

Fig. 5 is a flowsheet of the laboratory scale apparatus which was purchased from the University of Waterloo. Only the electrostatic precipitator is a new development from the University of Hamburg. Feedstocks tested were softwoods and hardwoods (particle size 0.3–0.5 mm) which were impregnated with different amounts of wood preservative such as CCB salts and creosote [20,21]. The temperature range studied is between 400–525°C, with 475°C giving the highest liquid yields of about 75% on dry feed. The fluidising gas is preheated nitrogen which passes from the bottom of the reactor through a distribution plate. Wood particles are fed pneumatically with a special stirred venturi-type feeder by a small stream of nitrogen from the top of the reactor through a tube directly into the hot fluidised sand bed of the reactor. Vapour gases and char particles leave the reactor at the top, a hot cyclone separates the char and two ice condensers collect the lower boiling molecules. The more stable aerosols (smoke) are precipitated in an electrostatic filter. The non-condensable gases are collected in a sample bag for analysis. Vapour residence time is about 1 s.

The oils from all the condensers are combined to a single product for analysis.

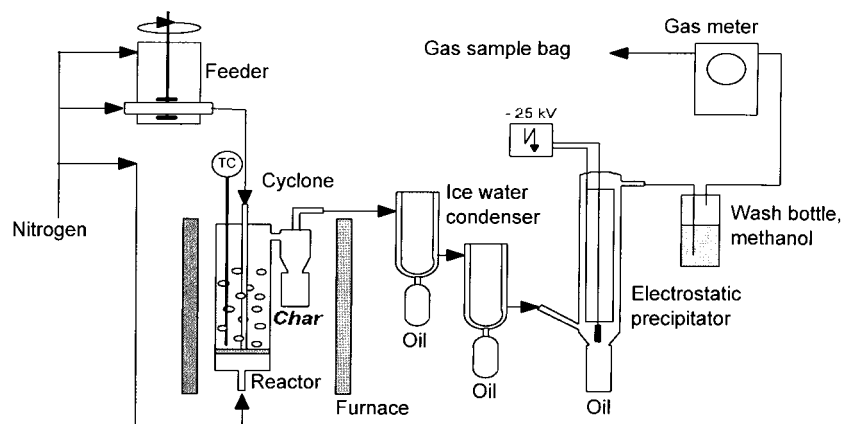


Fig. 5. BFH/IWC laboratory fluid bed.

The pyrolysis of softwood treated with CCB can be performed without any technical problems and the yields of the pyrolysis products are similar to those from untreated wood [22]. A typical mass balance is given in Table 8 with product analyses in Table 9.

4.3.3. Pilot plant

Fig. 6 is a flow sheet of the continuous fluidized bed pilot plant with the technology mainly based on the Hamburg process.

The feedstocks tested were cellulose, starch, softwood and hardwood. The feedrate is controlled by a vibration channel and the material is transported by a screw feeder into the reactor which has a capacity of 5 kg/h. Larger char particles which are not blown out of the reactor with the fluidizing gas fall into an overflow container. Fine char particles are separated by two cyclones. The vapours and gases then pass through two heat exchangers and an intensive cooler operating at -25°C . The stable aerosols finally pass through the electrostatic filters at a temperature of 1°C where they are completely precipitated. A piston compressor pumps the necessary gas volume for fluidization ($5\text{--}10\text{ m}^3/\text{h}$) back into the reactor and the excess gas is burned in a flare. With this condensation train four oils

Table 8
Typical mass balance (bench scale unit)

Inputs	kg	Outputs	kg	HHV, MJ/kg	% Energy
Dry biomass	100.00	Bio-oil	75	19.0	75.7
		char	15	26.5	21.1
		gas	15	4.0	3.2
Total	100	Total	100		100

Table 9
Typical product analyses

Liquid	
C (wt%)	50.2
H (wt%)	7.1
O (wt%)	42.7
Moisture (wt%)	18.0
HHV, MJ/kg	19.0
Copper recovery	95%
Chromium recovery	95%
Gas (wt%)	
CO	4.0
CO ₂	7.0
CH ₄	1.0
C+	3.0
HHV, MJ/kg	4.0

fractions are collected from the different condensers which are combined to give a total product.

4.3.4. Products

The product yields are summarised in Tables 10 and 11.

4.4. Bio-Alternative, Switzerland

4.4.1. Introduction

The primary objective of the process was charcoal production from which a by-product oil was derived by condensation of the vapours in the offgases. Although this was a carbonisation process, it was operated to give up to 20 wt% secondary

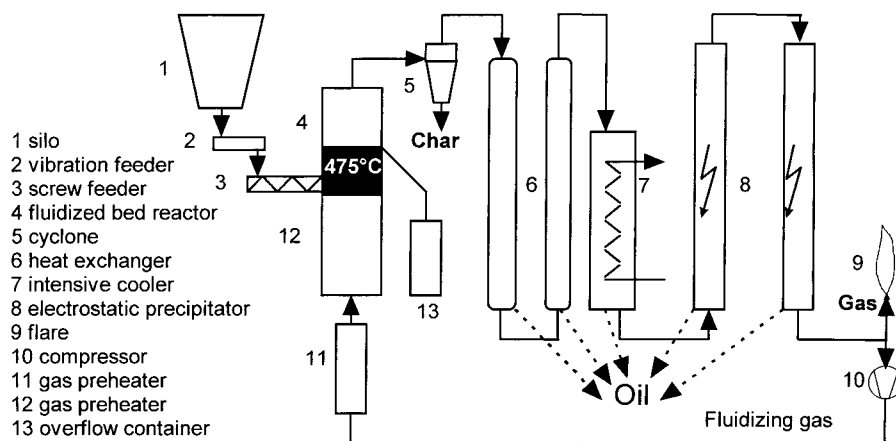


Fig. 6. BFH-IWC pilot plant flow diagram

Table 10
Typical mass balance (pilot plant)

Mass balance					
Inputs	kg	Outputs	kg	HHV, MJ/kg	% Energy
Dry biomass	100.0	Bio-oil	72.4	19.0	76
		char	14.35	26.5	21
		gas	13.25	4.0	3
Total	100	Total	100		100

liquids which, like the Alten process above, served to provide large samples of oil for testing and increased awareness of pyrolysis as a process for direct production of liquids from biomass.

A continuous 50 kg/h demonstration plant process was operated in Switzerland and several commercial plants have been sold up to 2 t/h feed capacity [23]. The oil from one of these large units in Spain was successfully utilised in a local hospital boiler. This also supplied oil for testing across Europe at the same time that the Alten plant was operating and served to both encourage interest in direct production of liquid fuels as well as to cause concern about the quality of the oil and the problems in handling and use from high viscosity and water separation. The product was a secondary oil from the long vapour residence times and high formation temperatures and thus had a high viscosity and low water tolerance leading to phase separation in some samples.

4.4.2. Description

Biomass such as wood, MSW, bark, sawdust, grape wastes, olive oil wastes and coconut shells, was comminuted and dried to a moisture content of 10–15% before being fed to the top of the reactor from a feed hopper.

The pyrolysis pilot unit was effectively a counter-current updraft partial gasifier for charcoal production. It comprised a vertical cylinder about 3 m high and 1 m

Table 11
Weight distribution of liquid in the condensation train

	Wt% based on total liquid yield
Heat exchanger 1	16.6
Heat exchanger 2	33.6
Intensive cooler	19.7
Electrostatic filter	20.4
Washing ethanol	9.7

in diameter. It was fitted with an interlocked twin feed hopper fed by screw feeder. A horizontal stirrer and a vibrator were used to prevent bridging of the feed in the reactor. The heat necessary for the reaction obtained was through internal combustion of part of the feed/char product, regulated by a system of air injection into the reactor through tuyeres.

Product gas left the top of the reactor at 120°C containing tar vapours and moisture. This was contacted with hot pyrolysis oil at 110–120°C which condensed the tar but left most of the water vapour in the gas phase. A sight glass was used to control the liquid level in the contactor and the excess liquid was periodically removed manually. The gas and water vapour were then burned in a boiler. As the oil is condensed at around 110°C, leaving most of the water in the vapour phase for combustion with the fuel gas, this solved the waste-water disposal problem associated with slow pyrolysis processes. Alternatively, the gas could be used for power generation. This requires further cooling by a heat exchanger to remove the water and tars present followed by filtration through a paper cartridge filter to remove tar traces. It was burnt in a 1.6 l modified Ford engine coupled to a generator. Char was removed through a rotary valve at the base of the reactor and through a water cooled screw for storage in plastic bags or steel containers.

4.4.3. *Products*

The charcoal yield was typically 30% wt on dry feed which is consistent with conventional carbonisation [23]. The oil yield was typically 15% wt on feed with no phase separation. It has been successfully fired in a boiler without any problems. Properties of the oil and gas are summarised in Table 12.

4.5. *BTG—Biomass Technology Group B.V. Netherlands*

4.5.1. *Introduction*

The Biomass Technology Group B.V. is an independent private firm of consultants, researchers and engineers which has its origin in the Chemical Engineering Department of the University of Twente. Their expertise covers a wide range of biomass energy technologies including pyrolysis, carbonisation, gasification, and combustion.

4.5.2. *Description*

The development of the rotating cone technology started in 1989 with a PhD research project at the University of Twente (q.v.) and resulted in a 10 kg/h prototype reactor [24]. It was continued in 1994 with another PhD project aimed at the development of a fully heat integrated laboratory plant and since 1996 with a subsequent project aimed at catalytic pyrolysis [25]. These activities have been described [26]. BTG owns the patent rights of the pyrolysis technology (patent no. PCT/NL/00327).

Meanwhile, up-scaling, pilot plant design and commercialisation is being carried out by BTG and Royal Schelde and Kara. As a first result, a 50 kg/h test unit has

Table 12

Bio-Alternative product analyses, see Ref. [23]

Liquid		Feedstock—Fir	Feedstock—Beech
Elemental composition	C wt%	58.12	55.10
	H wt%	6.55	7.20
	O wt%	34.81	35.10
	N wt%	0.52	2.00
	S wt%	—	0.6
	H/C ratio	1.35	1.56
	O/C ratio	0.45	0.47
Water content, wt%		4.5	14.0
Viscosity, cP		250@60°C	10@70°C
Net heating value, MJ/kg		22.2	20.9
Ash, %wt		< 0.05	—
pH		—	2.7
Density at 15°C, g/cm ³		—	1.216
Gas	Typical		
CO	16.3% vol		
CO ₂	13.2% vol		
H ₂	7.9% vol		
N ₂	48.4% vol		
O and H/C	14.2% vol		
HHV	3.8–5.5 MJ/Nm ³		
Solid			
HHV	30.0 MJ/kg		
Volatiles	12–18%		

been delivered to the Shenyang Agricultural University in China where co-operative research has been carried out for two years.

The development, construction and operation of another 50 kg/h bio-oil production unit has recently been contracted. This unit will be operational from July 1998 with an availability of 5000 h/y. Finally, a pilot plant with a throughput of 200 kg biomass per hour is being developed in an EC-FAIR programme.

BTG is involved in a range of EC and nationally funded projects to develop the technology for biomass, plastics and solid waste applications.

4.6. *Castle Capital Inc. Canada*

4.6.1. *Introduction*

Castle Capital Inc. is a holding company for several companies involved with fabrication of pressure vessels, military vehicle modifications and ship overhauls, as well as the recently developed biomass conversion process (see BBC for pilot plant tests). This is an oxygen free system using the Continuous Ablative Regenerator (C.A.R.) to convert solid and liquid organic wastes into high value

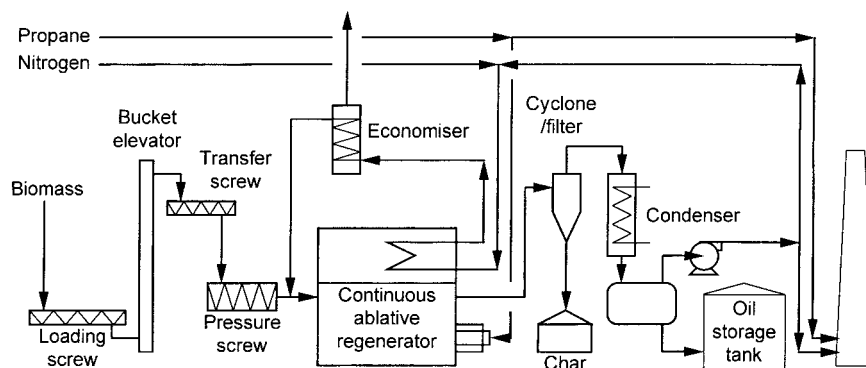


Fig. 7. Castle Capital continuous ablative reactor.

fuels and chemical feedstocks for utilization in, for example, a steam generator or a gas turbine.

4.6.2. Description

The 50 dry t/d C.A.R. System is illustrated in Fig. 7 [27]. This shows the preparation of feedstock to the reactor and a cyclone for coarse solids separation. A secondary bag or sintered metal filter can be added for smaller particle size removal down to $0.4\ \mu\text{m}$ giving a gas suitable for gas turbine operation. A condensation train for recovery of liquid fuel or for post processing follows gas clean-up.

The feedstock is injected into the pre-heated carrier gas at the inlet to the reactor with sufficient volume and velocity to sustain the movement of the feedstock and the products throughout the full length of the regenerator and through the downstream sections of the total C.A.R. System. The reactor is a hot plate system with indirect heating. Normal reactor operating pressure is in the range of 34.5 to 55.15 kPa. Some of the product gas is recycled to the reactor as carrier gas and for heating [27].

The secondary hot products filter allows recycling of the product gases to the reactor. The product gases not used as burner fuel can be used to produce electricity in a gas turbine or to dry feedstock. The vapours can be condensed to give liquids as chemical feedstocks for processing and recovery of the primary chemicals. If waste rubber is the feedstock, the condensed liquid may be used directly as fuels in diesel engines. Liquids from wood and RDF feeds require the addition of cetane. Gas turbines can burn the pyrolysis liquid if the fuel delivery system is modified to handle the low pH fuels.

A range of feedstocks has been tested in the bench scale C.A.R. System and in the 50 t/d demonstration plant in Nova Scotia. Emphasis is placed on wastes with a disposal credit but other feeds include oil recovery from oil shale, conversion of vegetable oils to higher value products, recovery of oils and gases from auto shredder wastes, refuse derived fuel, waste rubber and plastics. The process is not feedstock sensitive nor moisture sensitive because it does not have a heat transfer

medium (sand) to conduct the external heat to the feedstock. The plant has been mostly operated without vapour condensation and collection, and liquid product analyses and characteristics are not available.

4.6.3. Applications

The hot gases and vapours can be used to fire a steam boiler. Steam boilers can accept the hot product vapours and gases as produced at the low pressure of the C.A.R. System. The range of pressure is sufficient to deliver the gas into the boiler combustion cavity under controlled pressure conditions. If hot gases need to be delivered to a gas turbine, the reactor and system can be designed for operation at 2000 kPa at 500–700°C or higher if needed.

4.7. Colorado School of Mines, USA

4.7.1. Introduction

The objectives of the work were to produce pyrolysis vapours for catalytic treatment as a parallel study to the ablative pyrolysis work being performed at NREL using the same principle of contacting biomass with a heated surface under conditions of high relative motion and applied pressure. The work was fundamental in assessing the requirements for ablation and preliminary yield data was obtained. The work is significant in establishing some of the basic work on ablative pyrolysis.

4.7.2. Description

Reed and Cowdrey constructed a ‘heat flux concentrator’ initially to investigate ablative pyrolysis comprised of a drill press which forced and rotated wood dowels into a 1.2 cm diameter tapered hole in a heated copper block [28]. The vapours produced emerged through 12 holes in the bottom of the block and were condensed and collected in traps and a gas burette. The temperature range used was 500–700°C and total liquid yields of over 50% on an as fed basis were obtained. The forced contact of the wood with the concentrator however caused the holes to be plugged after about 10 g of wood was fed.

A ‘pyrolysis mill’ was then constructed as shown in Fig. 8 [28–31]. This second reactor was designed using the principles of a conventional mill for grain [30]. The pyrolysis mill consists of a stationary upper ‘stone’ and a rotating lower ‘stone’ which are both of copper and in contact with heaters. The lower plate is rotated at speeds up to 80 rpm, the pressure being controlled with a spring. The reactor wall is heated to 300–400°C to prevent pyrolysis vapour condensation inside the reactor. Wood particles enter the reactor through the upper plate and the vapours escape through the plate gap and then to a series of four liquid traps. Char and ash accumulate inside the reactor. Reed estimated the average heat flux in the first reactor to be 6.8 W/cm² and 5.08 W/cm² in the second reactor [31].

4.7.3. Products

Some results for the contact pyrolysis mill are presented in Table 13. Using this

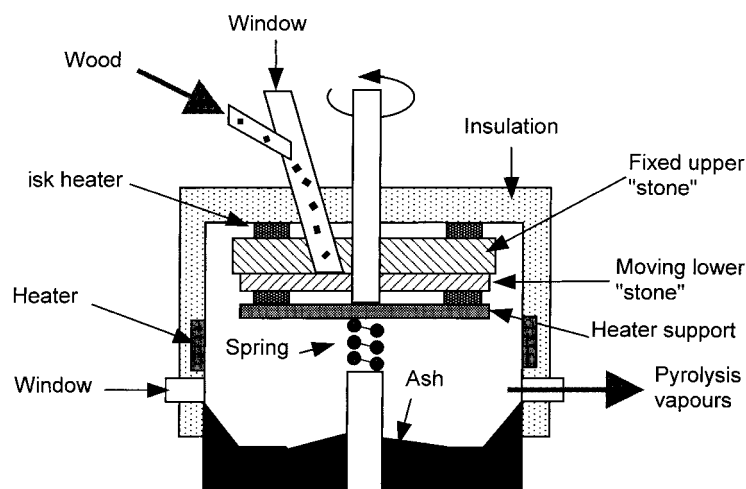


Fig. 8. Colorado School of Mines Ablative Pyrolysis.

reactor system, total liquid yields of up to 54% of liquid based on dry feed have been achieved. The only feedstock tested was bone dry wood. Feed rates of up to 0.2 kg/h were achieved with run times up to 1.5 h.

One of the main problems was the escape of the pyrolysis vapours through the plates due to plugging of the holes in the disc. Unreacted feed and char remains in the hot reactor environment where it undergoes more conventional pyrolysis. Scale up of this system could be difficult. No vapour residence time values are

Table 13
Some results for the ablative pyrolysis mill

Run number	105	109	111
Reactor temp (°C)	450	550	600
Throughput (g/h)	123.7	101.5	13.0
Char	58.3	18.0	5.5
Liquid	24.1	38.5	54.4
Gas (N ₂ /Ar free)	9.9	18.6	23.2
Gas composition (N ₂ /Ar free basis)			
H ₂	8.50	1.82	2.95
CO ₂	61.09	30.53	30.54
CO	29.29	48.92	44.39
CH ₄	1.00	12.47	14.81
C ₂ H ₄	0.00	0.12	3.11
C ₂ H ₆	0.00	1.63	1.88
C ₃ H ₆	0.11	1.32	1.71
C ₃ H ₈	0.02	0.33	0.31
1-butene	0.00	0.25	0.30
C ₄ H ₈	0.00	0.12	0.00

quoted. Cowdrey did not take into account the variation of the wood decomposition temperature with heat flux and reactor heated surface temperature as discussed by Lédé in his design study [32]. The concept is interesting, but the problem with using disks is that variable particle size causes processing problems due to disk spacing. Small particles will, therefore, not be under applied pressure and will more slowly carbonise on the hot plates. Reed suggests that an order of magnitude increase in pressure between the plates may overcome many of the problems including that of variable particle size [33]. Relative motion between particles and disk cannot be maintained as the particles tend to stick to one surface and not move as intended. Ribbed disks did not solve the problem. No further work has been carried out and the reactor has been dismantled.

4.8. CPERI, Greece

CPERI have been investigating the extraction and upgrading of phenolic components from fast pyrolysis liquids for several years. A small batch fluid bed pyrolyser has been operated for some time to produce liquids [34–37] for recovery of phenols for further processing including methyl aryl ethers as possible fuel additives [38,39] and anisole [40]. A range of chemicals has been extracted and derived [41]. The fluid bed has now been dismantled and an existing circulating fluid bed pilot plant is being modified for biomass fast pyrolysis with catalysts [42].

The batch fluid bed pyrolyser operated with 2 g feed and a particle size of 200–1000 μm at temperatures of 400–900°C and residence times of 5–40 s using an inert gas as fluidising medium and for control of vapour residence time. The unit was used for feedstock screening and operated at essentially atmospheric pressure. On-line gas analyses were performed and liquid analyses carried out by GC and GCMS [43]. The maximum liquid yield was 56 wt% and the maximum phenols yield was 12 wt%.

The circulating fluid bed pilot plant is an orthodox unit for studying FCC systems and includes a catalyst regeneration stage for burning off coke deposits on catalysts. This has been modified to accept biomass for fast pyrolysis and for catalytically enhanced pyrolysis. The vapours are cooled and separated. Reaction temperature is controlled by the catalyst flow from the regenerator to the reactor through a slide valve. The reactor temperature range is 300–600°C and the regenerator 500–700°C. Feed rates of 0.3–1.5 kg/h are possible with vapour residence times of 0.3–1.0 s. The reactor pressure is 1.6–3.3 atm. No results on biomass pyrolysis are available yet from this unit. A larger 35 kg/h unit has recently been commissioned.

4.9. CRES, Greece

4.9.1. Introduction

The Centre for Renewable Energy Sources, CRES, began a project on fast pyrolysis of biomass in spring 1990 as a consequence of the considerable

European interest generated in direct production of liquid fuels from the work of Alten and Bio-Alternative. This was one of six activities started at the same time in the EEC JOULE programme [44]—the others were Egemin, INETI, Union Fenosa, University of Aston and University of Twente, all of which are described in this review.

4.9.2. *Description*

The process has a nominal capacity of 10 kg dry wood per hour and is based on the principle that the by-product char from fast pyrolysis liquid production is used to provide process heat to drive the process. This is derived by burning the by-product char in a conventional bubbling bed at the base of the fast pyrolysis reactor to heat sand which is then carried up through a recirculating bed with the hot combustion gases to carry out fast pyrolysis in the riser section of the recirculating fluid bed [45]. Instead of having two separate reactors, as usually practised in steam and pyrolytic gasification processes, these are integrated into one vessel as shown in Fig. 9. The design is in line with the recommendations of the IEA Bioenergy Agreement liquefaction group of integrating char combustion into the flash pyrolysis reactor, and is an extension of the twin fluid bed and steam or pyrolytic gasification.

4.9.3. *Results*

After the commissioning runs, five runs have been achieved with good mass balance closures and full operating data availability [46]. Liquid yields of up to 61% wt on dry feed have been achieved as summarised in Table 14.

The system works well for short periods although the complexity of integrating a bubbling fluid bed char combustor directly with a circulating fluid bed pyrolyser cannot be underestimated. There are problems of long term operation and stability to be resolved as well as the dynamics of a close coupled cycling system. There are considerable benefits to be gained from such process integration in terms of cost saving and reduced heat loss, but at the expense of complexity and operability, neither of which have yet been satisfactorily demonstrated.

Liquid product yields are lower than those obtained for other fast pyrolysis processes. The deviations from 100% mass balance closures are due to loss of condensable organic vapours, either retained as solids–liquids agglomerates in the heat exchanger or escaping the cotton wool filter as unrecoverable aerosols. In addition there are minor uncertainties connected with the reliability of the volumetric biomass feeding system practised.

4.10. *Dynamotive, Canada*

Dynamotive was incorporated in 1991 and is currently located at BC research in Vancouver. The company is engaged in a variety of innovative technologies, notably fast pyrolysis for production of value added products derived from bio-oil including an emissions control sorbent known as BioLime[®].

A fluidised bed fast pyrolyser known as BioTherm[®], has been designed and

The pyrolysis liquid product provides material for producing a variety of Biomass Refinery products including value added chemicals and BioLime[®] which is the reaction product of whole or fractionated pyrolysis oil (bio-oil) and slaked lime (calcium hydroxide suspension). It is used for control of SO_x and NO_x in coal combustion systems.

Dynamotive is focussing on commercialising the biomass refinery concept through partnerships with industry leaders including Lockheed Martin/INEEL, Usina Santa Helena SA and Stone and Webster.

Table 14
Mass balances over the entire CFB reactor for the runs R7–R11

	Run number				
	R7	R8	R9	R10	R11
Operating Parameters ^a					
Riser temperature [°C]	581	605	579	496	550
Combustor temperature [°C]	678	700	645	748	740
Run time at steady-state [min]	30	28	45	31	45
Vapour residence time [ms]	374	388	396	458	373
Feedstock size, d_p [mm]	$1.5 < d_p < 2$				
Nominal air factor ($0 < S < 1$)	0.296	0.236	0.229	0.226	0.214
Final bed inventory [kg sand]	9.10	10.75	10.90	10.00	10.30
Input Streams (reactor)					
Biomass in [kg maf/h]	8.44	10.45	10.20	8.96	10.22
Moisture/ash in [kg/h]	0.73	0.91	0.89	0.78	0.89
Air in [kg/h]	16.00	14.70	13.90	12.10	13.00
Total feed in [kg/h]	25.17	26.06	24.99	21.84	24.11
Output Streams (reactor)					
Total liquids out [kg/h]	4.12	6.60	6.95	6.24	5.99
• recovered from HE ¹	3.31	5.12	5.18	3.87	4.13
• recovered from CWF ²	0.81	1.48	1.77	2.42	1.86
Total gas out/product gas [kg/h]	19.54	18.25	17.42	14.28	16.19
Gas composition [% wt]					
• N ₂	58.97	61.97	60.76	66.04	61.57
• CO ₂	20.43	24.13	28.15	26.97	27.12
• CO	14.58	9.75	7.84	5.18	8.81
• CH ₄	1.07	0.64	1.03	0.33	0.87
• O ₂	2.75	0.91	0.88	1.24	0.86
• C ₂ H ₆	0.11	–	–	0.02	0.07
• C ₂ H ₄	0.98	0.60	0.36	0.22	0.38
• Others (as C ₃ H ₆)	1.11	2.00	0.08	–	0.28
Totals Out [kg/h]	23.66	24.85	24.37	20.57	22.18
Mass balance closure [%]	94.00	95.36	97.52	94.18	91.99
Mass balance [N ₂ -free, %]	88.29	91.26	95.67	89.89	86.35
Total liquid yield [% wt maf]	40.12	54.46	57.43	61.50	49.91

^a 1—Heat exchanger (Fig. 9); 2—Cotton wool filter (Fig. 9).

4.11. Egemin, Belgium

4.11.1. Introduction

The aim of this process was the production of bio-oil by the flash pyrolysis of fine wood particles in a 200 kg/h vertical, downflowing entrained flow pilot plant shown in Fig. 10 [48,49]. The Egemin plant was commissioned in October 1991, part funded by the EEC from the Joule programme. The research was finished in 1993 and the project was abandoned due to lack of funding and less promising results. A basic problem of this plant was obtaining a sufficiently high rate of heat transfer in the short residence time needed for high liquid yields. This was one of two entrained flow reactors that have been researched (with GTRI), and abandoned.

4.11.2. Description

The feed was small wood particles of 1 and 5 mm. The reported feed moisture and ash contents are 16 and 0.57%, respectively. Wood was transferred from a

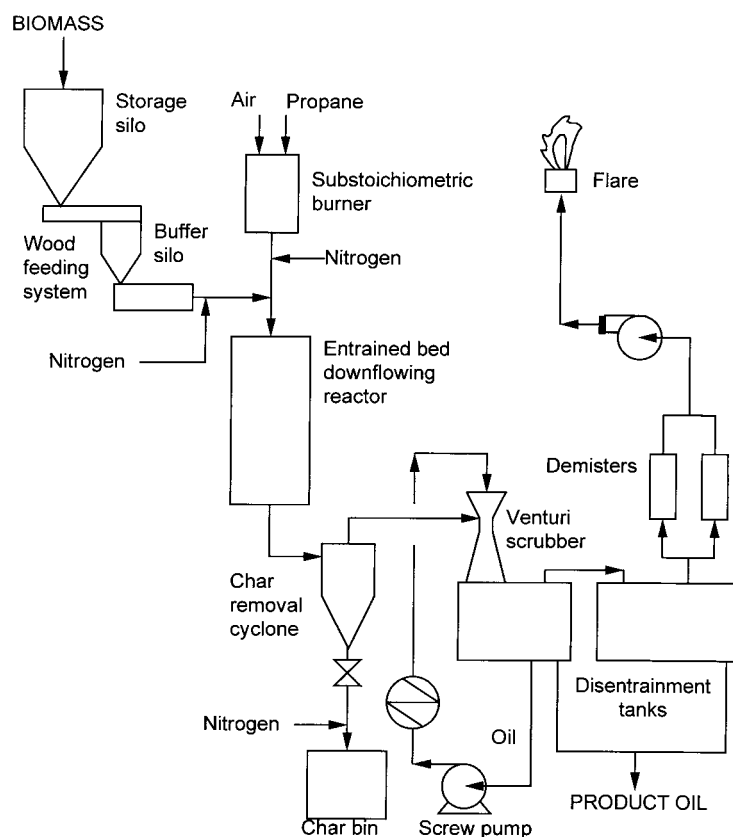


Fig. 10. Egemin flash pyrolysis process.

storage silo to a small buffer hopper before being fed into the reactor using a water cooled screw auger provided with a nitrogen purge. Wood particles were entrained into the down flowing vertical reactor (height 1.2 m, diameter 0.4 m) in a stream of hot gas at between 700–800°C produced by a 90% sub-stoichiometric burner fuelled by propane diluted with nitrogen to limit the temperature. The reactor was designed to give an average particle residence time of 0.6 s.

Pyrolysis products left the reactor at approximately 490°C and passed through a cyclone fitted with a nitrogen purge. The liquid products were separated by quenching in a venturi scrubber using product oil as the scrubbing medium. The vapour entry temperature to the venturi scrubber was approximately 400°C and the scrubber liquid exit temperature was 55°C during normal operation. The recycled oil was cooled with a water cooled heat exchanger. Mineral oil was used to start up the scrubbing system. The oil was allowed to accumulate in the disentrainment tank and was drained at the end of a run.

4.11.3. Products

A mass balance is given in Table 15. The gas mass flow rate was not measured and was obtained by difference. The bio-oil was collected from three points; the primary collection vessel, the secondary collection vessel and the drain at the fan.

During the operation, a number of problems have been encountered which has lead to the disappointing yields. The feed was not completely pyrolysed, particularly at high feed rates in excess of 100 kg/h which needs to be compared to the design capacity of 200 kg/h. This is likely to be due to insufficiently rapid heat transfer to the particles in the short residence planned as almost all heat transfer is by convection. Smaller particles would help to reduce this problem. The hot partially pyrolyzed wood continued to pyrolyse in the cyclone and char collection pot, potentially contaminating the primary flash products with secondary products. Egemin have suggested a recycle loop for the partially reacted feed which is analogous to the recycle loop in the NREL vortex reactor. Char carry-over from the cyclone collected in the liquid lines and caused blockages in the heat exchanger and pipework. Bio-oil separation from the non-condensable gas was poor as suggested by the poor bio-oil yields achieved to date (Table 15).

Table 15
Mass balance—Egemin flash pyrolysis process see Ref. [48]

	Mass flowrate (kg/h)	Yield (%)
Input		
Wood (dry)	84.0	—
Outputs		
Oil	33.5	39.9
Gas (by difference)	13.6	29.0
Char	24.4	16.2
Water	12.5	14.9

This is a common problem with most flash pyrolysis systems and conventional demisters do not appear to be effective.

An elemental analysis of the process products is shown in Table 16. The high quantities of hydrogen and oxygen in the char indicate incomplete reaction as discussed above.

4.12. Ensyn, Canada

4.12.1. Introduction

Ensyn's RTP[®] technology evolved from the research on fast pyrolysis carried out at the University of Western Ontario in the late 1970s and early 1980s. This had the main objective of employing fast pyrolysis to produce both gaseous and liquid fuels and chemicals although most of the publications from this work relate to ethylene and propylene production [e.g. 50,51]. The process was commercialised in 1989 [52]. The work on liquid products resulted in a commercial plant being sold to Red Arrow in the USA for recovery of food flavourings and additives [52,53].

There are currently eight operational plants: 30 dry t/d, 25 dry t/d and 3 dry t/d units at Red Arrow in Wisconsin, a 15 t/d demonstration plant at ENEL in Italy, a 100 kg/h unit, 40 kg/h unit and 10 kg/h R&D units at Ensyn in Ottawa, and a 20 kg/h unit at VTT in Finland. A number of facilities are currently at a design or construction stage at up to 350 t/d capacity. Ongoing development work includes hot vapour filtration to reduce ash and char, liquid filtration to reduce char, supply of oil for engine and turbine testing in Canada and Europe, combustion testing, upgrading and product characterisation.

4.12.2. Description

At least four reactor configurations have been developed, referred to as RTP-I, RTP-II [54], RTP-III and RTP-IV, some of which have variations. Fig. 11 shows the RTP-III configuration as designed for the ENEL Italian plant.

The heart of the system is a transported bed reactor which contacts hot recirculated sand with biomass in an upflowing reactor. In all the systems, biomass is comminuted to –6 mm and dried to not more than 10% moisture

Table 16
Process products—elemental analysis see Ref. [48]

	C		H		O		Ash		Total		HHV MJ/k g
	wt%	kg/h	wt%	kg/h	wt%	kg/h	wt%	kg/h	wt%	kg/h	
Bio-oil	0.39	13.3	0.08	2.7	0.53	17.4	0	0	1.00	33.4	18.04
Char	0.64	15.6	0.04	1.0	0.22	5.4	0.1	2.4	1.00	24.4	25.19
Gas	0.55	15.1	0.05	1.3	0.41	11.6	0	0	1.00	28.0	20.70
Total		44.0		5.0		34.4		2.4		85.8	

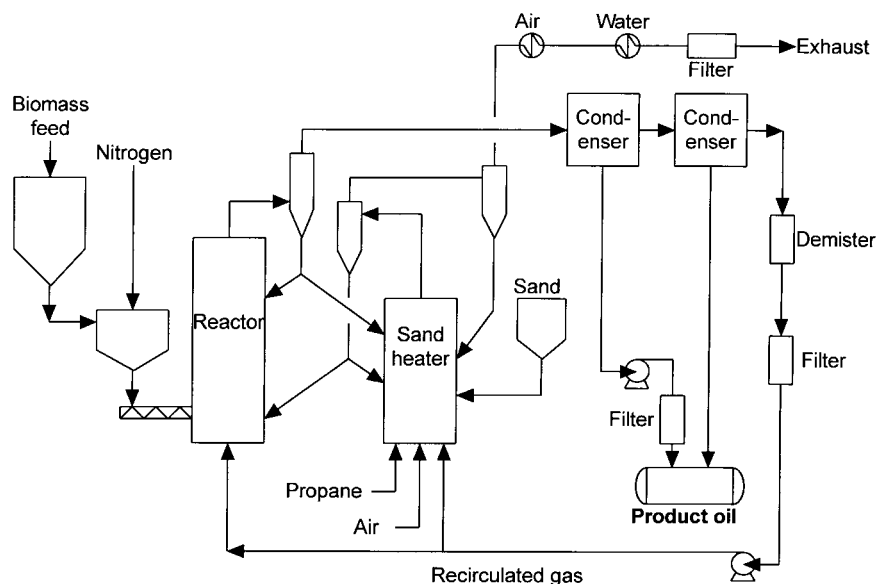


Fig. 11. Ensyn RTP III process flow sheet of the ENEL Bastardo plant [55].

before feeding to the reactor. The products are passed through two cyclones to separate solids, then the vapour is rapidly quenched and cooled in a multiple stage system. The total residence time for the hot vapours can be controlled down to a hundred milliseconds which 'freezes' the thermally unstable liquid intermediates of pyrolysis. These very low residence times are used for chemical production, while longer residence times are used for liquid fuels in order to more completely crack the lignin. R&D is currently underway to reduce the char and ash levels in the liquid by hot vapour filtration and oil filtration [56], as shown in Fig. 11.

A variety of feeds have been processed including cellulose on which much early work was carried out [57], wood, lignin, cellulose, sludges, agricultural residues, heavy oils, heavy distillates, asphalt and bitumen, and tyre crumb.

4.12.3. Product and yields

Characteristics of bio-oils can vary according to feed, reactor configuration [58] and process parameters [59]. From woody biomass feeds, the overall liquid yield is up to 83% by weight on a dry feed basis and has typical characteristics as listed in Table 17 [60,61].

4.12.4. Applications

The first commercial application of the Ensyn Technology was at Red Arrow Products in Wisconsin, USA which produce chemicals with the residual oil used as a boiler fuel [53].

Preliminary combustion tests performed showed that fast pyrolysis bio-oils could be used in place of heavy and light fuel oils in industrial boiler applications

[56,61] where bio-oil was shown to have a similar heat release rate and flame length as Number 6 fuel oil. More recent tests at Canmet [62] and at MIT [63] have shown that the liquid oil is more similar to light fuel oil in its combustion characteristics. Special combustion chambers would, therefore, not be required and a fossil fuel fired boiler or furnace could be easily converted to use this oil. Special attention has been paid to emissions, and one conclusion, for example, was that carbon monoxide emissions would be comparable to those from fossil fuel oil combustion, particulate emissions might be greater depending on the extent of char removal from the oil and NO_x emissions would be lower. SO_2 emissions from bio-oil combustion are less than 2% of those from the combustion of Number 6 oil. Bio-oil at Red Arrow is routinely burned in boilers for heat production [52] and has met local emissions requirements.

Currently Ensyn is working with a number of companies to test fire bio-oil in

Table 17
Wood derived pyrolysis oils from Ensyn

Physical property	Typical value	Range
Moisture content	22%	14–31%
pH	2.5	2.1–3.4
Specific gravity	1.18	1.16–1.22
Elemental analysis (moisture free)		
C	56.4%	55.3–63.5
H	6.2%	5.2–7.0
O (by difference)	37.1%	39.43–28.98
N	0.2%	0.07–0.39
S	< 0.01%	0.00–0.05
Ash	0.1%	0.04–0.25
C/H molar ratio	0.76	0.89–0.76
C/O molar ratio	2.02	1.87–2.92
HHV (moisture free basis)	23.1 MJ/kg	22.1–24.3
HHV as produced	17 MJ/kg	15–19
Viscosity (@40°C)	45 cp	35–55
Kinematic viscosity		
@25°C	233 cSt	
@40°C	134 cSt	
ASTM vacuum distillation		
160°C	10%	
193°C	20%	
219°C	40%	
Distillate	50°C	
Flash point	55°C	51–58
Pour point	–25°C	
Solubility		
Hexane insoluble	99%	
Toluene insoluble	84%	
Acetone/acetic acid insoluble	0.14%	

an internal combustion engine and is also involved in a large project with a gas turbine manufacturer to test fire bio-oil in a gas turbine [52].

Some costs and economics of the process have been published [56,64].

4.13. GTRI, USA

4.13.1. Introduction

This project was initiated in 1980 based on early research which showed that higher oil yields could be obtained from a rotating tube furnace with moving particles (typically 28 wt% liquid yield) rather than a stationary reaction bed (typically 17 wt% liquid yield) [65]. From this work, an entrained flow bed reactor was designed for the production of pyrolysis oil. This operated successfully until around 1989. Although apparently successful, the process was never scaled up. The only other entrained flow system for fast biomass pyrolysis was built by Egemin (q.v.). GTRI also developed the Tech-Air process which was similar to that of Bio-Alternative (q.v.) in that the principal product was charcoal with appreciable quantities of secondary oil derived as a by-product. This material was used extensively in early upgrading work.

4.13.2. Description

A process research unit was built and completed in 1983 [66–68]. In 1985, modifications were made so that optimisation of the oil yield could be further investigated, based on experience gained in the operation of the pilot plant and

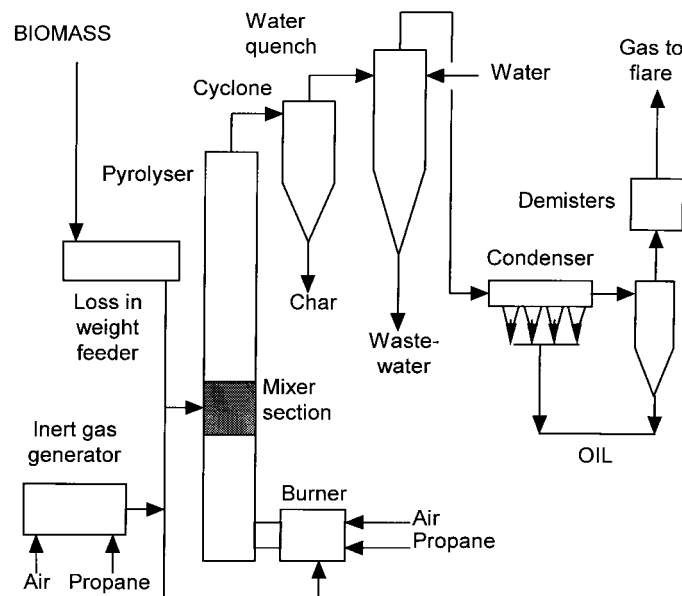


Fig. 12. GTRI pilot plant flow diagram.

the results of the commissioning runs. The major changes were the replacement of the 8 in diameter (20.32 cm) reactor tube with a 6 in (15.24 cm) tube, the addition of a quench vessel and a second demister [69–71]. The nominal operating feed rate was then 56.8 kg/h of dry biomass. Fig. 12 is a flow sheet of the process.

The feed is dried, hammer-milled to about 1.5 mm and fed from a loss-in-weight feeder into the reactor via a rotary valve. The reactor used is a 6 in inner diameter vertical tube made of stainless steel. The initial feed point was the refractory lined mixing section, located below the reactor tube. However, by introducing the feed into feed ports higher up the reactor, the effective length of the reactor could be reduced which in turn reduced the residence time. The wood particles are entrained in a stream of hot combustion gas (927°C) obtained by burning propane gas and air stoichiometrically. Gas and wood flow co-currently upwards through the reactor tube in which pyrolysis takes place; the resulting mixture consists of non-condensable gases, water vapour (moisture plus pyrolytic reaction water), pyrolysis oil vapours and char.

A cyclone separator is used to remove most of the char particles. The exiting gas stream consists of non-condensable gases, water vapour, pyrolysis oil vapours and some char fines. The hot effluent enters a water-sprayed quench vessel where it is rapidly cooled. Following the quench vessel, the mixture enters an air-cooled condenser in which the pyrolysis vapours are condensed with some water vapour. Early problems were reported with accumulation of tarry material in the first stages of the air-cooled condenser.

The condensed phases are removed via sumps and receivers and the gaseous product is passed through two demisters connected in series. Most of the aerosols present in the gaseous product are removed in the demisters. The remaining effluent, consisting of non-condensable gases, water vapour and remaining aerosols, enters a flare where it is burnt and the combustion products are exhausted to the atmosphere.

In the scaled up process, it was intended that waste water production would be minimised or eliminated by controlled cooling and condensation of oil to retain the water in the vapour phase with subsequent combustion of the water laden by-

Table 18
GTRI product yields (modified reactor)

	Run number				
	2–11/0	2–12/0	3–17	3–18	3–19
Reactor temperature, °C	501	524	499	504	500
Yields (% wt dry ash free feed)					
Oil (total liquid)	48.1	53.8	52.1	60.0	54.9
Char	7.6	8.4	10.0	12.1	21.2
Total gas ^a	44.3	37.8	37.9	27.9	23.9

^a By difference.

product gas for process heat. There was, however, no experience of internal gas recycling in the pilot plant.

4.13.3. Product

Table 18 shows some of the last results with liquid yields approaching 60 wt% on feed [72]. Modelling and optimisation studies produced predictive models which indicated that yields of 70 wt% would be achievable with a well designed reactor and system. The oils are highly oxygenated with no phase separation as shown in Table 19. They have an initial boiling point range from 70 to 90°C. They are heat sensitive and will decompose when heated to temperatures greater than 185–195°C. The oils are acidic, have an acrid odour and also exhibit corrosive properties with some metals. The product was upgraded by hydrotreating at Battelle PNL [73] which is discussed in more detail in that chapter. The liquid was also upgraded in the liquid phase over zeolite cracking catalyst—the only known application of this approach to zeolite cracking which is usually carried out on freshly produced vapours. The results have not been published, but extensive coking is understood to have occurred.

4.14. Interchem Industries Inc., USA

4.14.1. Introduction

Interchem Industries Inc. was founded in 1985 from work carried out at Pyrotech Corporation. Early work was to scale up an ablative fast pyrolysis process to solve an energy deficit problem at a pulp mill at Samoa, California [75,76]. In 1989 the company entered into a consortium to develop and exploit the commercial potential of the NREL ablative pyrolysis process (see above) to produce a phenol adhesive substitute and an alternative fuel [77].

Although there were some early attempts to demonstrate the principles of

Table 19
Typical bio-oil analysis from GTRI [74]

Elemental Analysis (wet basis)	
C (% wt)	39.5
H (% wt)	7.5
N (% wt)	< 0.1
S (% wt)	—
O (% wt)	52.6
H/C ratio	2.28
O/C ratio	1.00
Moisture (% wt)	29.0
Ash (% wt)	0.2
Char content (% wt)	27–31
Viscosity, cp@60°C	10
HHV, MJ/kg	24.3
Density, g/cm ³	1.23

pyrolysis in a vortex type reactor, the first significant plant was built in Springfield, Missouri for the conversion of sawmill wastes. Construction of the 32.7 t/d facility for the production of fuel oil and charcoal, referred to as a Petroleum Synthesis Unit, was completed in September 1990 and this was tested until 1992 [78,79]. The plant was redesigned and relocated to Kansas and a new reactor was built based on the NREL vortex ablative reactor. This second plant was never completed and the project has been abandoned.

4.14.2. Description of Springfield plant

The reactor wall was heated by the combustion of recycled non-condensable pyrolysis gases. The product vapours from the reactor were directly quenched in a 6 tray column, initially using diesel and then product liquids. The collected liquids were split: part was recycled to the quench column and the rest was transferred to a storage tank. The remaining gases and uncondensed vapours were recycled to the reactor furnace where part was combusted for process heat.

The design capacity of 1360 kg/h was not achieved and throughputs of only 90 kg/h were initially achieved at the Missouri site due to the problems noted above. The process had some operational difficulties concerning particle handling, notably particle recycle problems, particle carryover into the product collection system, low particle velocities in the reactor leading to low throughputs and plugging of the plate heat exchanger [80].

Various modifications were then made to the process including replacement of the plate heat exchanger with a shell and tube exchanger to remove the blockage problems, rebuild the recycle loop in order to retain the particle kinetic energy and improve the process efficiency and placing the reactor exit cyclones in series to improve particle collection efficiency. These modifications and repairs only increased the throughput to 180 kg/h, 13.2% of the design capacity. The reasons for the low throughput were then surmised to be due to loss of particle velocity upon entering the reactor due to the initial 0.6 m of the reactor tube not being heated, i.e. the particles were experiencing dry friction and consequently lost a significant proportion of their velocity; the recycle gas was not sufficiently reheated in the condenser and the recycle loop was becoming overloaded with unreacted particles.

No quantitative results of the operation of the Springfield first plant have been published. The plant was closed down in late 1992 and decommissioned as the problems could not be solved using the existing equipment. The pretreatment and handling units have been retained as they worked as expected and the heat exchanger on the liquids recirculation system has been improved. Interchem relocated the wood handling equipment to Kansas City and built a second reactor based on the NREL ablative vortex reactor (see above).

A new reactor was designed by NREL based on their work (see above) and was to have been incorporated into the relocated plant in Kansas. The new process is shown in Fig. 13 [81]. This was due for restart in late 1993, but has been abandoned.

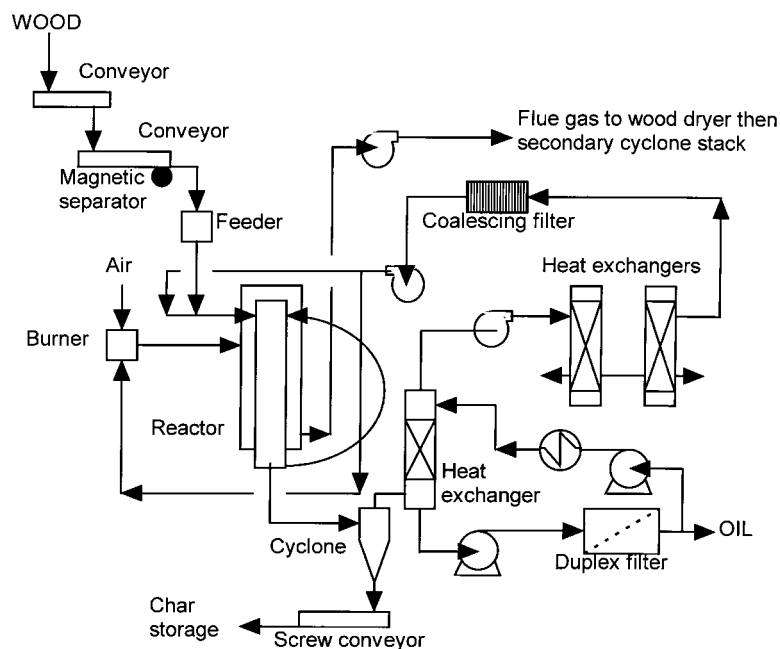


Fig. 13. Second generation Interchem petroleum synthesis process, Kansas, 1993.

4.15. National Renewable Energy Laboratory, USA

4.15.1. Introduction

The original aim at the beginning of the 1980s was to convert biomass into non-equilibrium olefinic gases in a low pressure process without the addition of a catalyst in an analogous concept as the later work at the University of Western Ontario which led to the formation of Ensyn (q.v.). This aim was modified in 1984 to produce liquid fuels in high yield employing a close coupled catalytic (zeolite) reactor system to generate hydrocarbon fuels such as gasoline, BTX, and chemical fractions such as phenolics.

Interchem (q.v.) attempted to modify the concept of the NREL vortex reactor in their first pilot/demonstration plant at Mountain View, MO, USA, but this was not successful. The second attempt was based on the NREL designed ablative vortex reactor, an example of which is shown below. While the reactor was built, the completed plant was never operated and the project is understood to have been abandoned by Interchem.

NREL has upgraded their original pilot plant in Golden to enable real time on-line analysis of pyrolysis and gasification products. A slightly larger second unit was built and operated to produce barrel quantities of hot vapour filtered pyrolysis oils. This second unit has recently been mothballed. There is more recent work on fluid bed fast pyrolysis [82], on MBMS fast pyrolysis [83] and on close coupled riser zeolite upgrading (see later).

The description below focuses on the ablative vortex reaction system as the major R&D activity in fast pyrolysis.

4.15.2. Description

Initially a smooth walled vortex reactor with a gas-solids recycle loop, made from Inconel 800 H in order to withstand temperatures of 1000°C was used. However, early experimentation demonstrated that severe coke deposits were formed at wall temperatures much above 650°C [84]. Since a lower reactor temperature of 625°C was needed, a vortex reactor made from 316 stainless steel was designed, constructed and tested. The reactor has a diameter of 13.4 cm and a length of 70 cm. The reactor is heated externally by three-zone electric cylindrical furnaces. To force the particles into tighter helical paths than would naturally occur, a helical rib having a pitch of 25 mm and width and height of 3 mm was machined from the wall of the reactor. An insulated recycle loop was added tangentially at the exit of the reactor to recycle partially pyrolysed feedstock and any large char particles.

Very high organic vapour yields resulted from this lower wall temperature operation. The original design capacity of the vortex reactor was 50 kg/h biomass but the maximum throughput achieved to date is 36 kg/h [85–87]. Development efforts have focused on product quality rather than reactor throughput.

Fig. 14 shows the configuration of the reactor system up to around 1990. The reactor was then installed vertically and a hot vapour filter added in 1995 as shown in Fig. 15 [88]. Most recently the unit has been used as a high temperature pyrolytic gasifier also with the hot vapour filter where the char acts as a cracker thereby reducing the tar in the gas [89]. Biomass, with a particle size of about

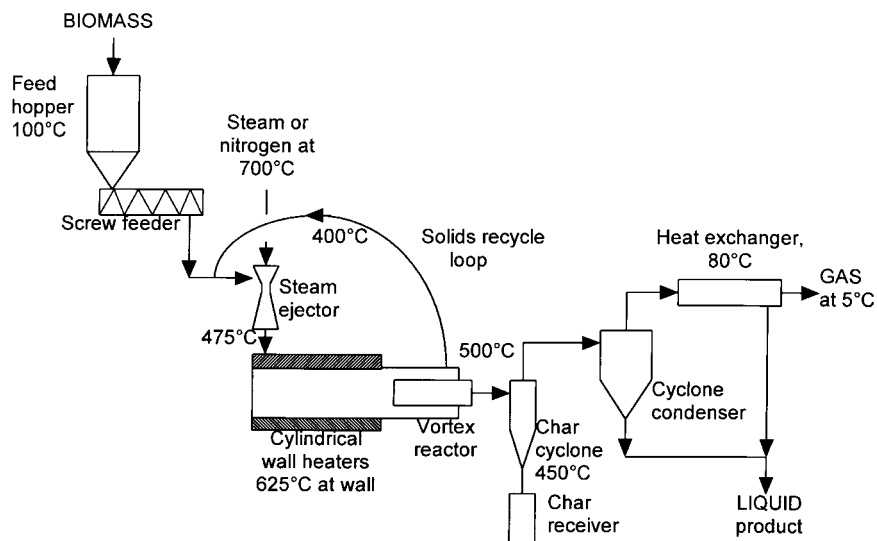


Fig. 14. NREL pilot plant flow diagram in original configuration.

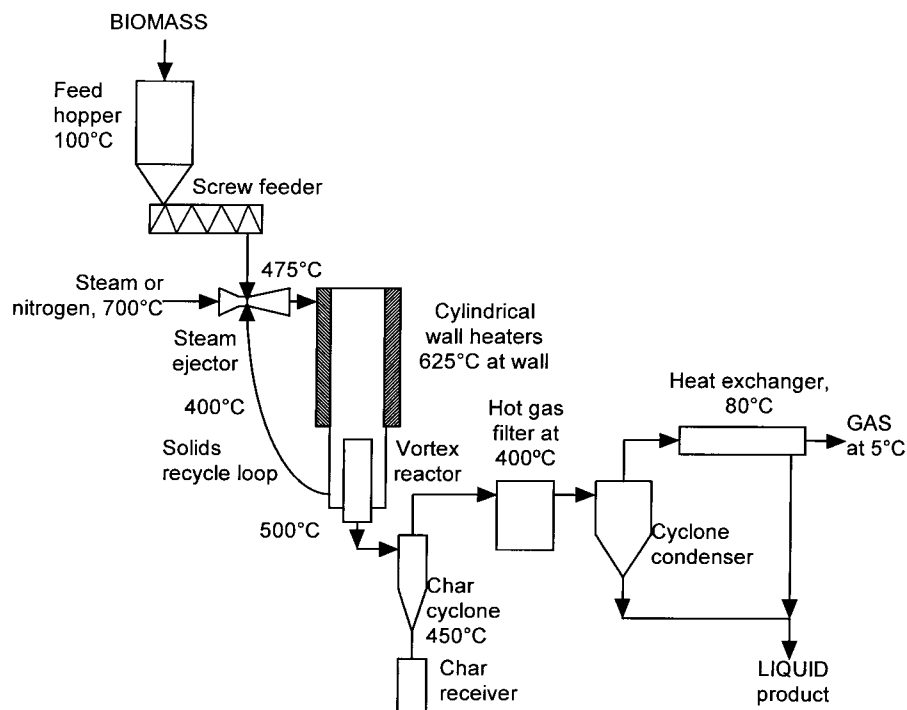


Fig. 15. NREL pilot plant flow diagram in latest configuration.

5 mm, is metered into the system, where it is entrained and mixed with the recycle stream. The biomass particles, entrained in the carrier gas, enter the vortex reactor tangentially at speeds of up to 400 m/s so that the particles are forced to the reactor wall by high centrifugal forces.

The fine char, gases and vapours in the reactor leave through the axial exit which extends part way into the reactor. The reactor has a very high specific capacity and can in principle be easily scaled up. Very high heat transfer rates are achieved between the hot wall and biomass particles sliding against the hot reactor wall.

The wall temperature has to be limited to a maximum of about 625°C to ensure production of a liquid film between the wall of the reactor and the particle which then vaporises and leaves the reactor. The product stream then passes through a char cyclone or baghouse where the char is removed. The cyclone diameter is 4 in (10 cm) and operates at 475–500°C.

Recent efforts to produce a cleaner pyrolysis oil by hot filtration of the pyrolysis vapours have been very successful in preventing char fines from being collected with the pyrolysis oil condensates. This has reduced the ash content of the oil to below 0.01 wt% and the alkali content to a few ppm. The colour of the hot gas filtered oil is brown rather than black.

The vapours pass to the first heat exchanger which is a 38 cm diameter cyclone.

The condensed liquids and water are retained in the receiver. The cooled gas stream at about 80°C is then passed to a blower and a series of heat exchangers before passing through a coalescing filter, an orifice meter, and then to a flare.

4.15.3. Products

Using this experimental layout, oil yields of 67% wt (including moisture on a dry feed basis) or 55% (dry oil on dry feed basis) have been obtained with 13% wt (on a dry feed basis) char.

The liquid obtained is highly oxygenated, dark brown in colour and acidic with a pH between 2–3. If nitrogen is used rather than steam as the carrier gas, a single homogenous phase is present at water contents below about 25%. Small samples of the oil have appeared to be stable at room temperature for a prolonged time but exothermic reactions will occur if the temperature of the oil is raised to 100°C or more. The fresh oil vapours have been found to irritate the eyes and the nose; however they were not carcinogenic with cancer-prone mice. Analytical data is given in Table 20.

The phenol fraction has been successfully extracted and polymerised with formaldehyde to form plywood resin and other resins. A consortium of companies including Interchem (q.v.) was formed to commercially exploit the phenolic recovery process [90] but the lack of pyrolysis oil from Interchem has limited this development.

While RDF has been successfully pyrolysed, problems arose from deposition of highly viscous condensate (having a melting point of around 80°C) in the first heat exchanger, which required extensive modification of the condenser train [91,92].

The char from wood has a volatile content of 15–45%, a bulk density between

Table 20
Analysis of pyrolysis liquids from the NREL process [93]

	Run 175 (poplar feed)	
	Wet basis	Dry basis
Elemental Composition, wt% on feed		
Carbon	46.5	57.3
Hydrogen	7.2	6.3
Oxygen	46.1	6.3
Nitrogen	0.15	0.18
H/C ratio (atomic)	1.86	1.32
O/C ratio (atomic)	0.74	0.47
Ash	< 0.01	< 0.01
Moisture	18.9	0
Viscosity, cp	18@40°C	
Heating value, MJ/kg, HHV	18.6	23.0 ^a
LHV ^a	17.0 ^a	21.6 ^a

^a calculated.

0.18–0.24 g/ml and a higher heating value of 33 MJ/kg. The empirical formula is $\text{CH}_{0.53}\text{O}_{0.12}$.

4.16. Pasquali-ENEL, Italy

Within the context of an EC sponsored project, Pasquali and ENEL are collaborating on the development of a circulating fluid bed fast pyrolysis system with a nominal capacity of 150 kg/h, referred to as CIRO [94]. This is based on modification of a CFB combustor and includes integral char combustion at the base of the pyrolysis riser. The plant is still undergoing development and results are not yet available.

4.17. Pyrovac, Canada

4.17.1. Introduction

The Pyrocycling[®] process is the product of research carried out by Dr Christian Roy and his research team originally at the Université de Sherbrooke (1981–1985) and then at Université Laval (1985–today). In 1988 Dr Christian Roy created Pyrovac Institute Inc., a private research and development centre which is devoted to developing the process and improving the products obtained from various industrial wastes. In 1996 the engineering firm Pyro Systems Inc. was created and is responsible for the scale-up of the process. The Pyrocycling[®] process is being commercialized by Pyrovac International Inc., a Canadian company created in 1990 whose business office is in Montréal, Canada and whose shares are being held 50:50 by Ecotechniek b.v. and Pyrovac Group Inc. Ecotechniek b.v. is controlled by UNA, a large Dutch utility company, and is responsible for a wide variety of environmental activities in The Netherlands. Pyrovac Group Inc. is also the holding company of Pyrovac Institute Inc. (100%) and Pyro Systems Inc. (100%) and its head office is in Québec City, Canada.

4.17.2. Description

The patented process involves the thermal decomposition of organic materials under specific conditions such as reduced pressure, heating rate and temperature in order to produce useful products. The process is typically carried out at a temperature of 450°C and under a total pressure of 15 kPa. These conditions enable the recovery of large quantities of pyrolytic oils as well as solid carbonaceous materials which possess distinct surface properties.

The feedstock is introduced under vacuum after drying and shredding into the reactor known as the Pyrocycler[®], a specially designed integrated equipment system shown in Fig. 16. The feedstock is conveyed over two horizontal plates which are heated by a mixture of molten salts that are maintained at a temperature of 530°C. The hot salts are heated by means of a burner which is supplied with the non-condensable gases produced during the pyrolysis process. An electrical induction heater is optionally used to maintain a constant temperature inside the reactor. When heated, the organic matter in the feedstock

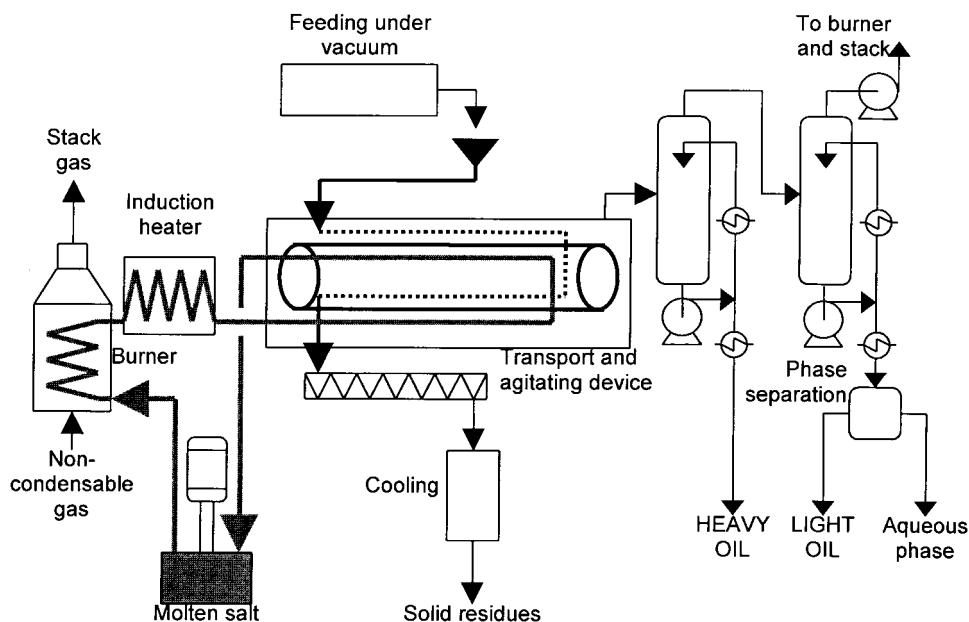


Fig. 16. The Pyrocycling[®] vacuum pyrolysis process.

decomposes into vapours which are rapidly removed from the reactor by means of a vacuum pump. These vapours are then directed to two condenser units in which the heavy and light oils are recovered together with an aqueous phase. The residual solid products are cooled at the reactor outlet. There is an extensive bibliography of which a few key references are included [95–97].

4.17.3. Products

Typical yields of pyrolysis products obtained during the vacuum pyrolysis of biomass species are given below in Table 21.

4.17.4. Applications

Promising commercial applications in the short term include biomass, used tires and sewage sludge. Other applications are also being developed for the recycling of automobile shredder residues, biomedical wastes, waste plastics, municipal solid wastes, petroleum sludges and other industrial wastes with organic components. In most cases, the wastes are completely transformed into pyrolysis oils, water, solid residues and non condensable gases. The process can be used for the remediation of soils contaminated with hydrocarbons or to extract bitumen from tar sands.

4.17.5. Integrated Pyrocycling[®] combined cycle (IPCC)

The combustion of vacuum pyrolysis biomass products through an Integrated Pyrocycling[®] Combined Cycle (IPCC) system can result in 18–30% increase of electricity output per ton of biomass compared to direct biomass combustion. The

Table 21
Typical yields of vacuum pyrolysis products

Typical yields (wt%, dry wood basis)		
	Fir/Spruce bark	Spruce wood
Pyrolysis oils	35%	47%
Pyrolytic water	20%	17%
Wood charcoal	34%	24%
Gas	11%	12%
Fir/Spruce bark pyrolysis oil		
Elemental comp. (wt%, @23% moist)		
C	55.4	
H	8.4	
O	35.3	
N	0.6	
S	< 0.01	
Ash	0.3	
Density, kg/m ³ @25°C	1140	
HHV, MJ/kg	23.0	
Water, wt%	23.0	
Viscosity @50°C, cSt	5.6	
Flash point, °C	> 95	
V, Na, pm	each: < 1	
Ca, ppm	107	
K, ppm	22	
pH	3	
Wood charcoal		
HHV, MJ/kg	30.4	
Volatile matter	20.3	
Ash	7.6	
Fixed carbon	72.1	
Gas composition (vol%)		
Hydrogen	6.6	
Methane	10.0	
Carbon monoxide	32.0	
Carbon dioxide	41.5	
Ethane	1.5	
Ethene	1.5	
Propene	1.4	
Propane	0.4	
Methanol	0.4	
Butane	0.4	
Butene	0.6	
Pentane	0.6	
Others	3.1	
HHV, MJ/kg	10.9	

The thermal efficiency for electrical generation purposes is 26%. The IPCC uses the flue gas from the charcoal boiler for biomass drying which contributes to the overall process efficiency.

The vapours formed during the vacuum pyrolysis of the biomass are rapidly withdrawn from the unit by a vacuum pump system and are quickly condensed. The pyrolytic oil product is burned in a gas turbine which is connected to a steam generator (HRSG). All this energy is converted in a 40% efficient combined cycle for the generation of 8.5 MWe of electricity while the excess energy is also used to provide heat to the dryer. The non-condensable gases are burned to provide up to 50% of the energy required for the pyrolysis process. A small fraction of the wood oil is used to provide the remaining 50% of the energy needed. To convert the original biomass into pyrolytic products, the Pyrocycling[®] process itself requires 3.1 MW_{th} which is available from the process products as described above. The total electricity production is 14.0 MWe.

4.18. Resource Transforms International Ltd, Canada

RTI was established in 1992 by former employees of University of Waterloo Department of Chemical Engineering, led by Prof D. Scott to exploit possibilities of production of speciality chemicals by pyrolysis.

RTI has considerable experience in pyrolysis, with over 70 different feedstocks and over 20 process configurations. Small scale equipment for pyrolysis is designed, constructed and units sold to several universities and research laboratories in Europe and Australia. Assistance has also been provided to Union Fenosa, in the development of their 200 kg/h pilot plant.

Research quantities of speciality chemicals such levoglucosan and its derivatives are manufactured, purified and sold to synthetic and pharmaceutical chemists [98,99]. Other speciality chemicals and pyrolysis liquid derived products have also been produced [100,101].

The personnel of RTI have been involved in fast pyrolysis research since 1980 and have published well over a 100 papers on the subject, not including a dozen or so patents e.g. [102–104].

In May 1996, RTI and Dynamotive Corporation announced partnership and collaboration in the field of 'biomass refinery'. RTI agreed to grant to Dynamotive exclusive license to its patented pyrolysis process. Such exclusivity was contained to emission control applications only.

RTI currently operate an in-house designed 20 kg/h fast pyrolysis reactor with energy integration and a recent patent has been granted [105].

4.19. Stenau, Germany

The Stenau process is based on the work carried out at the University of Tübingen. There is little information about technical aspects of the process other than that a rotary kiln is used to slowly pyrolyse refuse/MSW at fairly low temperatures to effect partial liquefaction at a capacity of 1 t/day refuse [106–108].

Table 22
Summary of Stenau process

Feedstock throughput (d.a.f.)	1 tonne/day
Liquid product yield	0.309 tonne bio-oil/tonne feed
Gas product yield	71 m ³ /tonne feed
Solid residue yield	0.56 tonne/tonne feed

The performance is summarised in Table 22. The liquid yield is about 31% wt on dry MSW feed with 71 m³ of gas per tonne feed, some of which is used for process heat, and a solid residue of 56% wt on feed. The plant is understood to be still operating in 1995, but no recent information is available.

4.20. TWT (*Thermal Wood Treatment*) Inc, Canada

A 200 kg/h fluid bed reactor derived from the University of Waterloo work was originally constructed in 1986 by Encon for wood and peat pyrolysis. This was taken over by TWT in 1993 for processing old telegraph poles. The unit was constructed as a totally self-contained plant on the back of a trailer for transportation to test sites for demonstration.

Old telegraph poles had their outer skin of treated wood removed which was then pyrolysed in the fluid bed pyrolyser at around 50 kg/h for recovery of chemicals including creosote and PCP for recycling. The reaction temperature was relatively low for pyrolysis at around 350–400°C suggesting that distillation played an important role. Up to 30,000 poles per year were processed. The skimmed poles were re-treated and recycled [109]. No information is available on performance or costs. The plant was closed down in 1996.

4.21. Union Fenosa, Spain

4.21.1. Introduction

Union Fenosa undertook the construction of a substantial pilot plant in 1989 for the production of pyrolysis liquids for fuels. After a thorough review of available technologies at that time, a license was agreed for the Waterloo Flash Pyrolysis Process (WFPP) developed by the University of Waterloo in Canada (q.v.).

Construction of the 200 kg/h plant started in 1990 and commissioning began around October 1992. By mid 1993 the unit was operating reasonably satisfactorily at 160 kg/h dry wood throughput, although some problems with liquid collection had to be resolved [110]. Work is continuing on developing the process and considering scale-up to 2–4 t/h [111,112]. The plant has supplied researchers and organisations in Europe and North America with both laboratory and commercial sized samples for evaluation and testing in a variety of applications including combustion and engines. A number of extensive

modifications have been carried out in the past year to improve several aspects of the unit's operation and performance.

4.21.2. Description

The flowsheet is shown in Fig. 18 [112]. After storage the feed is ground then dried with surplus recycled gas supplemented with propane. While most work has been carried out on eucalyptus due to its local preponderance, other feeds have been tested including oak and pine. A cyclone removes fines prior to venting the combustion products to atmosphere. The dried feed is stored in a closed hopper prior to metering to the fluid bed pyrolyser. The fluidising gas is recycled gas which is heated with a propane fired heat exchanger.

The product char is separated in a cyclone and stored in a closed container. In the initial design, the vapours are cooled in two water cooled heat exchangers in series, then passed through a demister and a final cooler to remove as much oil as possible. This part of the plant has seen substantial modifications and details are still proprietary. All liquid product streams are combined.

The plant has been undergoing extensive modification from summer 1996 to early 1998 involving improvements to the feeding system and liquid collection system.

4.21.3. Products

Detailed mass and energy balances and product analyses are not available at this time, but reported char yields of around 20% wt on dry feed [113] are closer to 15% [114]. Oil yields of up to 70% wt on dry feed have been indicated [113]. The early operational difficulties in producing a consistent quality of oil from eucalyptus have now been mostly solved and the plant is producing a consistent but relatively viscous liquid with a water content of 15–25 wt%. Pine and oak feeds have also been tested recently.

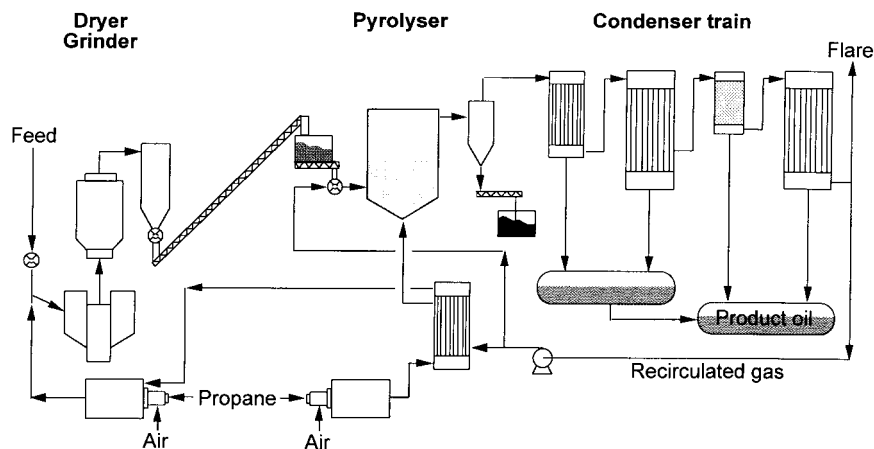


Fig. 18. Union Fenosa pilot plant 1995–1996.

4.22. University of Aston, UK

4.22.1. Introduction

A novel ablative plate pyrolysis reactor has been designed, constructed and operated for the production of liquids in high yields from wood feedstock under a range of operating parameters, primarily reactor temperature and residence time. The process concept has been successfully demonstrated at 3 kg/h and oil yields of up to 80% wt on dry feed have been obtained. A scaled up version is being developed.

Several fluid bed reactors are also available supplied by Waterloo University and RTI which are not described here [115].

4.22.2. Description

Fig. 19 shows the simplified reactor unit used as an example of a laboratory scale R&D unit to study principles and design new concepts [116]. Ablative pyrolysis is one of the most extensively researched methods of fast pyrolysis [117]. The underlying principles are the use of high applied pressure of the biomass particle to be pyrolyzed onto a hot surface at not more than 600°C while moving it at a high speed (>1.2 m/s) relative to the hot reactor surface. In the Aston process, the biomass particles are pressed onto a flat heated metal surface using

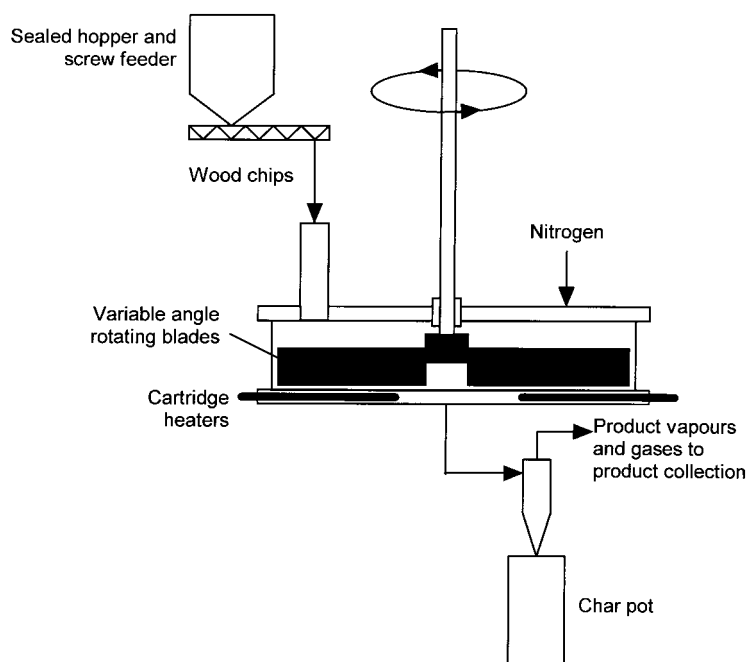


Fig. 19. Aston University ablative pyrolysis reactor: simplified schematic.

angled blades which also impart horizontal movement of the particles across the hot surface.

Dried biomass particles of up to 6.35 mm are fed into the nitrogen purged reactor from a sealed purged screw feeder. Four asymmetric blades rotating at speeds up to 200 rpm generate a mechanical pressure on the particles, pressing the particles onto the heated reactor base, typically heated to 600°C. The mechanical action of the blades causes the particles to pyrolyse (thermally erode) under the conditions of high relative motion to the heated reactor surface. The product vapours and gases are removed from the reactor with the diluting nitrogen and the char is removed in a cyclone.

It is important to note that nitrogen purging and the use of any inert gas is not required, but is added in the laboratory tests for control purposes such as safety in the feeder and residence time control in the reactor.

The primary liquids are recovered in a counter-current quench column with final stable product vapours in the non-condensable gases being removed by an electrostatic precipitator. The remaining gas is passed through a gas meter before discharge. A small sample is periodically removed for on-line gas analysis up to C₄.

4.22.3. Products

Table 23 gives some results from four runs using poplar wood feed. The

Table 23
Results for the ablative pyrolysis reactor—ablative pyrolysed wood basis [118]

	Run number			
	CR07	CR11	CR06	CR10
Reactor surface temperature (°C)	550	550	600	602
Gas/vapour temperature (°C)	389	294	415	368
Wood H ₂ O (wt%, dry basis)	2.44	1.86	9.25	1.99
Residence time(s)	2.83	1.97	6.92	1.71
Ablative char (wt%)	14.3	13.8	14.8	15.7
Organics (wt%)	58.1	55.7	51.8	66.1
H ₂ O (wt%)	22.7	18.3	28.2	11.5
Total liquids	80.8	74.0	80.0	77.6
Gas (N ₂ free, wt%)	9.0	8.2	10.4	6.2
Gas yields (wt%, moisture free feed)				
H ₂	0.01	0.06	0.00	0.04
CO ₂	3.53	3.80	4.86	1.71
CO	3.65	2.55	3.83	3.38
CH ₄	0.33	0.21	0.39	0.20
C ₂ H ₄			0.12	0.07
C ₂ H ₆			0.07	0.06
C ₃ H ₆			0.37	0.00
C ₃ H ₈			0.00	0.03
Closure	101.1	95.8	105.3	99.5

product has many of the attributes of fast pyrolysis liquids but appears to be more stable i.e. the physical properties do not change as quickly as some products from other fast pyrolysis processes. Samples have been kept for over two years with little apparent change. This phenomena requires more extensive testing as well as the development of suitable stability tests for confirmation.

This work is continuing with new heat transfer relationships being derived and further experiments carried out at a range of reactor temperatures and residence times. A second generation system is under development.

There is associated work on catalytic pyrolysis, biomass pretreatment, chemicals recovery from bio-oil, physical property measurement and test method development, and techno-economic assessment of fast pyrolysis systems.

4.23. University of Leeds, UK

4.23.1. Introduction

Both fixed and fluid bed reactors have been operated for fast pyrolysis and disposal of wastes, with catalytic upgrading of the products in the case of the fluid bed work. The objective has been to carry out screening studies on feedstocks, products; examine the effect of zeolite catalysts; and particularly examine the production of noxious products that may mitigate against implementation.

4.23.2. Description

A 200 ml stainless steel fixed bed reactor has been used to pyrolyse tyres. The reactor is externally heated and nitrogen is used as a carrier gas. Heating rates up to 80°C/min and temperatures from 300–720°C [119]. More recently, work using polystyrene as the waste has been carried out with secondary thermal cracking of the product vapours at 500, 600 and 700°C [120]. Experiments were also carried out with a third catalytic cracker using ZSM-5 catalyst maintained at 400°C which lowered the proportion of styrene oligomers but increased the proportion of PAH. Work has also been carried out on fixed bed catalytic upgrading of model compounds as a prelude to the pyrolysis of biomass.

Model compounds such as furfural, cyclopentanone, anisole, ethylacetate and methanol were upgraded over 10 g ZSM-5 in a fixed bed using nitrogen as a carrier gas and a range of temperatures ranging from 300 to 500°C, WHSV 4 ± 0.5 [121]. The results showed that the Effective Hydrogen Index (EHI) was important in determining the conversion to other products. As the EHI increases for each model compound, the degree of mass conversion also increases. The importance of this is that it was estimated that the products of wood pyrolysis would have a lower degree of mass conversion compared to liquids produced from RDF or rice husks. For biomass liquids with an EHI number less than 1, a catalyst at 500°C would produce a liquid with the lowest oxygen content. For biomass liquids with an EHI greater than 1, a catalyst at 400°C would give optimal conversion.

Subsequently, a dual fluid bed was used to pyrolyse biomass. Biomass was pyrolysed in an externally heated 0.075 m diameter bed, 1 m high with nitrogen as

the fluidising gas. Part of the reactor freeboard was packed with ZSM-5 catalyst. Liquids were collected before and after pyrolysis for comparison. Selected results are given below for yield of oxygenated compounds from biomass pyrolysis.

4.23.3. Products

For both reactors, the liquids were recovered and analysed by GC/MS. Analyses for biomass derived liquids both with and without zeolite catalysts are shown in Table 24. Quantification of PAH was performed by GC/FID. The recovery of styrene from the polymer was $53.0 \text{ wt}\% \pm 1\%$ at cracking temperatures of 500 and 600°C decreasing to $34.0 \text{ wt}\%$ at 700°C . The effects of metal salts on the pyrolysis of cellulose have been studied in a fixed bed reactor and by TGA [122].

For tyres, the maximum yield of liquid was obtained at $80^\circ\text{C}/\text{min}$ and 720°C with a yield of $58.8 \text{ wt}\%$ liquids, $14.8 \text{ wt}\%$ gas and $26.4 \text{ wt}\%$ char. Detailed analysis of the liquids by SEC, FTIR have been performed.

In zeolite cracking, the conversion of oxygenates in the pyrolysis vapours occurs at lower catalyst temperatures to H_2O and CO_2 and CO at higher catalyst temperatures [123]. Coke formation on the catalyst was typically $11.4\text{--}13.1 \text{ wt}\%$, although the run times over which this occurred are not quoted. A key feature of

Table 24

Oxygenated compounds from biomass pyrolysis with and without zeolite catalyst (mg/kg biomass fed)

Name	No catalyst	Catalyst temperature, $^\circ\text{C}$			
		550	400	450	500
Acetic acid methyl ester (T)	5195	0	0	0	0
Acetic acid propyl ester (T)	6800	0	0	0	0
2-cyclopentan-1-one	3825	2630	1430	1005	710
Methylcyclopentanone	745	830	510	350	240
Furanone	3042	0	0	0	0
Methyl furfural	600	435	90	50	40
Phenol	1055	1310	1340	1170	1080
Benzenediol	235	565	220	110	25
2-hydroxy-3-methylcyclopentanone	1840	760	200	110	45
Methylfuranone	470	0	0	0	0
Methylphenol	1785	2360	1885	1605	1590
Methoxyphenol	1935	1070	705	175	170
Dimethoxyphenols	850	2140	2115	1670	1295
Ethoxyphenol	2690	1795	1145	585	275
Methylbenzenediols	1375	1590	1125	915	330
Trimethylphenols	1045	1825	1840	905	550
Methoxypropylphenols	5060	3145	825	500	340
Naphthenols	0	0	315	350	330
Methylnaphthenols	0	0	440	310	280
Dimethylnaphthenols	0	0	240	123	100
Dimethoxypropenylphenols	3421	2230	420	80	70

zeolite upgrading is the significant level of PAH formed which requires careful handling and thorough processing to meet current safety requirements [124].

4.24. University of Tübingen, Germany

4.24.1. Introduction

The objective of this research is to convert biomass such as sewage sludge, agricultural wastes and refuse/MSW into fuels or raw materials for the organic chemicals industry as an alternative solution to landfill and incineration of sewage sludge [125,126]. Several batch and continuous laboratory scale plants up to 5 kg/h have been built and tested. The principle is to use low temperatures of less than 350°C and long reaction times of up to one hour to achieve low oxygen content oils and high yield of fine chemicals. The concept has been licensed to several organisations in Europe (Stenau q.v.), North America (Wastewater Technology Centre q.v.) and Australia (Wastewater Technology Centre q.v.) and several plants of up to 2 t/h are planned or operating based on sewage sludge.

4.24.2. Description

At a laboratory scale, both batch and continuous screw reactors have been used. Sludge, dewatered to about 20% wt solids, or other biomass, is heated slowly to 300–350°C in an oxygen free environment for about 20 min, and the liquid product collected in an ice-cooled bath. No additives are needed as the silica, silicates and heavy metals present in the sludge are claimed to act as catalysts. The vapour is condensed and collected. Feedstocks tested include sewage sludge, rape, lupine and Euphorbia.

Four types of equipment have been used on a larger scale for low temperature conversion. These are: a rotary furnace (up to 80 kg/h); a fluidised bed, (up to 400 kg/h); a reactor with a transport belt for MSW conversion (up to 200 kg/h) and a cone screw converter for the conversion of agricultural wastes.

4.24.3. Products

Oil yields ranging from 18 to 27 wt% (feed basis) and char yields from 50 to 60 wt% (feed basis) have been achieved. Table 25 shows the elemental analysis of the products.

Liquids with very low oxygen content (less than 5% wt oxygen) have been reported from a sewage sludge feed. The low oxygen level and chemical intermediates are claimed to be due to low reaction temperature, natural catalysts in the feed and slow reaction times. The oils contain aliphatic hydrocarbons and fatty acids as the main components [127].

Organic halogenated compounds such as chlorinated dibenzodioxins and dibenzofuranes are destroyed and organic chlorine is converted into hydrochloric acid [128].

The sewage sludge derived oil has been reported as being used as fuel for a diesel engine.

Table 25
Elemental analysis of products from University of Tübingen [129]

	Oil	Char	Water vapour	Product water
C	72.62	35.05	0.59	4.33
H	10.75	2.92	11.54	10.53
N	1.27	1.24	0.09	0.35
Cl	0.06	1.08	–	0.06
S	0.24	–	0.15	0.14
O (by difference)	15.06	8.59	87.63	84.59
Others	–	51.12	–	–

4.25. University of Twente, Netherlands

4.25.1. Introduction

Gas–solids reactors, such as fluidised bed processes, have been studied for a long time within the Chemical Reaction Engineering group. One direction focuses on the development of new reactor types including the rotating cone reactor. Several projects have aimed at further development of the rotating cone technology for pyrolysis.

This work was instigated to develop a new intensive reactor technology for the pyrolysis of biomass by sliding and pressing the particles on a heated surface. The original aim was to achieve ablative pyrolysis where the particles ‘slide’ across a heated metal surface in a rotating cone, but subsequent development of the initial ideas led to a type of transported bed pyrolyser.

The development of the rotating cone pyrolysis reactor took place in two European sponsored research projects from 1989 to 1997 [130–134]. Current research is concerned with the development and testing of the new concept in the framework of a European Joule-project on catalytic pyrolysis. Special attention will be paid to the in-bed catalytic upgrading of the bio-oil and the first experimental results were recently obtained in this new concept.

4.25.2. Description of Concept 1

The rotating cone is a novel type of reactor, applicable to fast pyrolysis of solid materials. The concept is that biomass particles are fed onto an impeller which is mounted at the base of the heated rotating cone together with an excess flow of inert (or catalytically active particles). These are then flung on to the heated surface to be pyrolysed while being transported spirally upwards along the hot cone wall. The concept is depicted in Fig. 20. The final char ash residue is ejected from the top of the cone. No carrier gas is needed, which reduces the size and costs of the secondary oil-collection system considerably. The reactor is very compact and has a very high solids transport capacity of up to 3 kg/s solids.

Initial experiments were carried out mainly with a cone temperature of 600°C and a cone rotational speed of 900 rpm. The reactor interior was subsequently modified as shown in Fig. 21 to reduce the operational volume from 0.25 m³ to

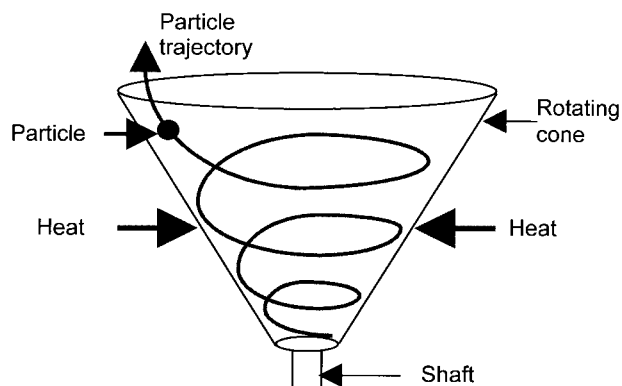


Fig. 20. University of Twente rotating cone principle.

0.003 m³, otherwise the gas/vapour residence time would be around 80 s giving significant vapour cracking. The reactor outside the cone quickly becomes filled with sand and char, restricting experimental runs to 10 min. The liquids are collected in a condenser/quench system [135]. The reactor was subsequently modified to permit internal sand recycling as shown in Fig. 22.

The reactor has been further modified so that the sand is removed from the reactor with the char, the char combusted and the hot sand re-fed to the reactor, i.e. an internal sand recycle. A cold model was constructed at the beginning of

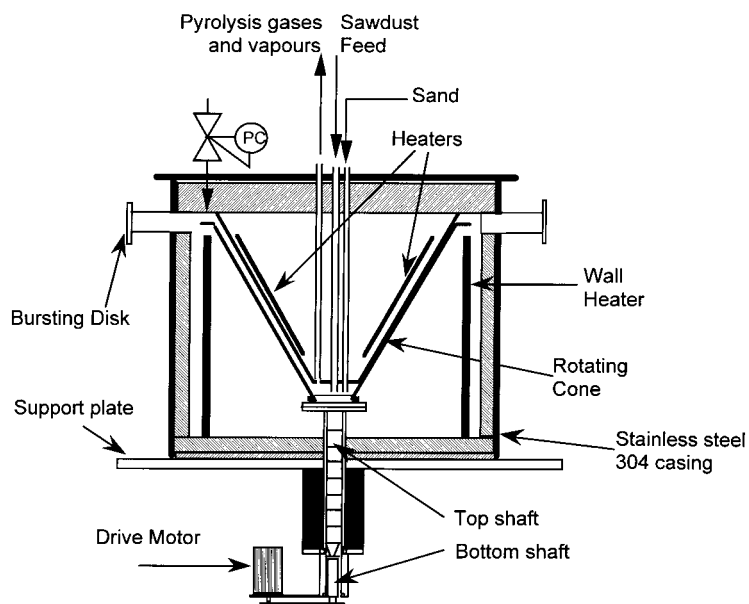


Fig. 21. University of Twente rotating cone flash pyrolysis reactor.

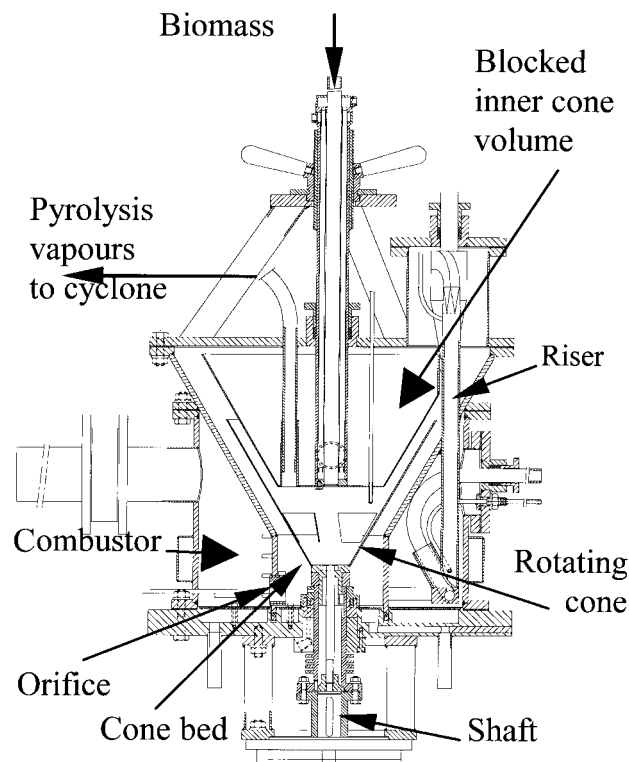


Fig. 22. Energy integrated rotating cone pyrolysis reactor.

1995 and has subsequently been tested as a hot system. The latest arrangement is shown Fig. 22.

Another project is aimed at the recycling of plastic waste by flash pyrolysis in another bench-scale unit, also based on the prototype rotating-cone concept by Wagenaar [136]. In this project the 'back to monomer' concept is experimentally studied on a pilot plant scale, and the aim is to produce high value monomers from short heating-up times and rapid quenching conditions. Technical and economic evaluation of the entire process have indicated that the rotating cone reactor is very competitive with other types of gas-solids reactors such as bubbling fluid bed and riser systems.

4.25.3. Products

Isothermal reactor operation leads to significant cracking of the product vapours. Typical yields at 1 s residence time and a heated surface temperature of 600°C are: 60 wt% liquids; 25 wt% gases and 15 wt% char. The mass balance closure is generally around 90%. Work is also in progress to devise tests for measurement and prediction of bio-oil thermal stability.

4.25.4. *Future plans*

A second reactor is currently being developed to provide internal circulation of the sand with reheating by combustion of by-product char. Scale up to 200 kg/h biomass feed is being implemented by BTG (q.v.) in co-operation with KARA.

4.26. *University of Waterloo, Canada*

4.26.1. *Introduction*

This programme was initiated in the early 1980s with the main objective of establishing conditions for maximising liquid yields from biomass, particularly from forest materials. The University of Waterloo can be credited with the foundation of modern fast or flash pyrolysis. Their research is probably the most extensively published and publicised in this area; for example [137–142].

Initially, a bench scale continuous flash pyrolysis unit using a fluidised bed at atmospheric pressure was employed. The reactor conditions used were feed rates of up to 50 g/h with a particle size range between 140 and 60 mesh (between 105 and 250 μm) in a nitrogen atmosphere over a temperature range of 400–650°C. Results indicated that at an apparent vapour residence time of 0.5 s, organic liquid yields of 60–70% (moisture free) could be obtained from hardwoods such as aspen, poplar and maple while yields of 40–60% could be obtained from agricultural wastes such as wheat, straw, corn stover and bagasse. Using the results obtained from the bench scale unit, a larger process unit of 3 kg/h was designed, constructed and tested. This has been extensively studied and a 200 kg/h pilot plant based on results from this unit has been constructed in Spain by Union Fenosa (q.v.).

Most of the personnel from the fast pyrolysis group have formed a company—Resource Transforms International whose activities are described above.

4.26.2. *Description*

A flow diagram of the 3 kg/h process unit at Waterloo is shown in Fig. 23. The wood is air dried (to 7% moisture), hammer milled and screened to a particle size of $-595\ \mu\text{m}$ (-30 mesh). The wood is then conveyed from a hopper by a variable speed twin screw feeder into a cavity where it is conveyed into the reactor by recycled product gas. The feed injection point is within the bed itself. The reactor bed material is sand and the fluidising agent is recycled product gas (a $\text{CO-CO}_2\text{-CH}_4$ mixture) which is preheated in the inlet line by controlled electric heaters. In addition, the reactor is wrapped with heating coils allowing extra heat to be added either to the bed of sand or to the freeboard space. The feed hopper and feeder are mounted on a hinged platform resting on a load cell, and hopper weight loss is continuously recorded.

The fluid bed was designed to entrain the char and blow it from the bed while retaining the sand. This is done by careful selection of sand size biomass particle size, bed velocity and reactor configuration. This is called the ‘blow-through’ mode of operation since there is a negligible amount of char present in the sand and hence there is no need for sand circulation or replacement.

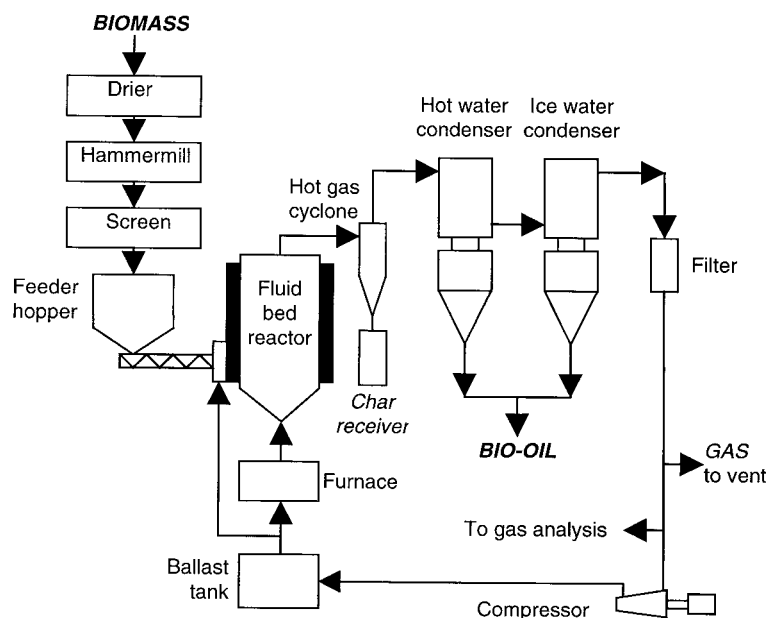


Fig. 23. University of Waterloo pilot plant flow diagram.

The reaction temperature (from 425 to 625°C) is controlled by a thermocouple within the fluid bed which regulates the inlet gas heating coils. The reactor pressure of about 1.25 bars (125 kPa) absolute is monitored by differential and absolute bellows type gauges. Throughputs from 1.5 to 3 kg/h have been used.

The reaction products pass through a cyclone where char is removed. The vapours and the gaseous product pass through two condensers in series. These condensers are vertical and have pyrolysis gas inside the tubes; each condenser has a clean-out plug at the top and a condensate collection pot at the bottom. The first condenser is held at about 60°C while the second one uses chilled water at around 0°C as the cooling medium. Tarry products are collected in the condensers. The effluent gases then pass through a filter to remove tar mist and then to a recycle compressor. A proportion of this gas stream is taken from the compressor discharge and used to fluidise the reactor bed and convey feed into the reactor, while the excess is vented through a gas analyser and gas meter as product gas. The product gas is analysed for CO and CO₂ in an on-line infra-red gas analyser-recorder. Samples of the product gas are also taken periodically and analysed by gas chromatography.

4.26.3. Products

High yields of liquid product were obtained at temperatures around 500°C which is believed to be due to minimum secondary decomposition reactions occurring at such low temperatures (see Table 26). The liquid product is highly

Table 26
Reported pyrolysis yields from different woods at optimal conditions

	Brockville Poplar	White Spruce	Red Maple
Temperature, °C	504	500	508
Moisture content, wt%	5.20	7.00	5.90
Particle top size, mm	1000	1000	590
Apparent residence time, s	0.47	0.65	0.47
Feed rate, kg/h	2.10	1.91	1.98
Yields, wt% (dry wood basis)			
Water (reaction product)	9.70	11.60	9.80
Char	16.50	12.20	13.75
Organic liquids (dry)	62.90	66.50	67.90
Gas composition (wt% dry wood basis):			
CO	4.71	3.82	4.12
CO ₂	5.89	3.37	4.89
H ₂	0.02	0.02	0.01
CH ₄	0.44	0.38	0.36
C ₂ H ₄	0.19	0.17	0.16
Others	0.25	0.04	0.26
Total Gas	11.50	7.80	9.80

oxygenated with no phase separation. It has a low viscosity and contains 10–20 wt% water depending on the moisture content of the feedstock and the reaction temperature employed. It is dark in colour with an acrid smell. The liquid is quite stable at room temperature over a twelve month period. Some properties of the liquid product are outlined in Table 27.

The gas produced has a higher heating value of about 14.4 MJ/Nm³. This value increases at higher reaction temperatures as the CH₄ content increases and the CO₂ content decreases.

Table 27
Properties of pyrolytic liquids

	Brockville Poplar	White Spruce	Red Maple
Elemental analysis			
C	54.70	54.00	54.70
H	6.90	6.80	6.40
O (by difference)	38.40	39.20	38.90
H/C ratio	1.51	1.55	1.40
O/C ratio	0.53	0.54	0.53
Water content (wet)	18.70	22.40	18.00
pH	2.40	2.10	2.40
Density, g/cm ³	1.20	1.22	1.19
Higher Heating Value, MJ/kg	23.20	22.70	22.40

4.27. Wellman Process Engineering

4.27.1. Introduction

Wellman have a long history of thermal conversion of both coal and biomass. A novel oxygen donor biomass gasifier was constructed jointly with John Brown Engineers and Constructed in the mid 1980s and an updraft biomass gasifier with advanced tar cracking system is commercially available. At 250 kg/h biomass fed fast pyrolysis fluid bed pilot plant is currently under construction supported partly by the European Commission (shown in Fig. 24).

4.27.2. Description

The unit is provided with a continuous biomass system to allow continuous and long term operation. The reactor is an orthodox bubbling fluid bed which is heated by combustion of by-product char in an annular fluid bed combustor with most heat requirements being met through the reactor wall. The product vapours are passed through two cyclones before being quenched with cooled recycle product oil. The vapours are finally passed through an electrostatic precipitator. The unit is under construction with a planned start-up of later 1999. The product yield is expected to exceed 70 wt% liquids with a moisture content of typically 25%.

5. Liquid product characteristics

Fast pyrolysis liquid has a higher heating value of about 17 MJ/kg as produced with about 25% wt water that cannot be separated. The liquid is often referred to as 'oil' or 'bio-oil' or 'bio-crude' although it will not mix with any hydrocarbon liquids. It is composed of a complex mixture of oxygenated compounds that have been 'frozen' in cracking and re-formation from the rapid cooling that integral to

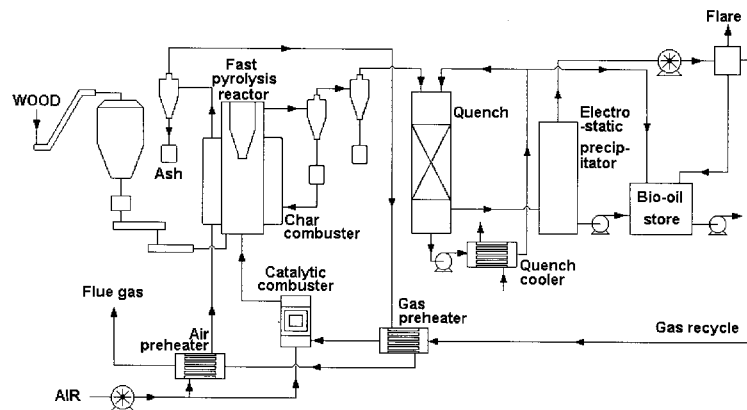


Fig. 24. Wellman process Engineering Fluid Bed Fast Pyrolysis Pilot Plant.

the fast pyrolysis process, and this complexity provides both the potential and challenge for utilisation. There are some important features of this liquid that should be emphasised which are described below and the main properties are typified in Table 28 and summarily characterised in Table 29.

5.1. Water

Water is miscible with the bio-oil up to around 30–45% and it is important to note that bio-oil is not miscible with fossil fuels. The water that is produced in the pyrolysis reaction together with any water contained in the feed reports to the liquid product. The amount of water in the product also depends on the process parameters including the extent of secondary reaction or cracking and the temperature of the product gases leaving the liquid collection system. When substantial gas flows are involved in the process such as with fluid bed type reactors, considerable water is lost as saturated vapour in the exit gas as well as losses from light ends. Water is important in many ways—increasing water usually reduces viscosity, improves stability and reduces heating value.

Table 28
Typical properties and characteristics of wood derived crude pyrolysis oil

Physical property	Typical value
Moisture content	15–30%
pH	2.5
Specific gravity	1.20
Elemental analysis	
C	56.4%
H	6.2%
O	37.3%
N	0.1%
Ash	0.1%
HHV as produced (depends on moisture)	16–19 MJ/kg
Viscosity (at 40°C and 25% water)	40–100 cp
Solids (char)	1%
Vacuum distillation	max 50% as liquid degrades
Characteristics	
• Liquid fuel	
• Easy substitution for conventional fuels in many static applications—boilers, engines, turbines	
• Heating value of 17 MJ/kg at 25% wt water, is about 40% that of fuel oil/diesel	
• Does not mix with hydrocarbon fuels	
• Not as stable as fossil fuels	
• Quality needs definition for each application	
• Standards required	

Table 29
Characteristics of bio-oil

Characteristic	Solution
Water content	Product is hydrophilic to an extent, optimise for application
Instability	
Temperature	Do not heat above about 80°C
Oxygen	Avoid contact with air
Light	Avoid light
Water	Complex
High viscosity	Careful heating, not above about 80°C. Add water and/or co-solvents
Char, suspended	Filter vapour or liquid. Modify char or application
Low pH	Careful materials selection
Alkali metals	Contained in char so filter, pretreat feed to remove ash
In-homogeneity	Change or modify feed, modify process conditions, add additives
Health and safety	Proper precautions for toxicity

5.2. pH

The degradation products from cellulose include organic acids such as formic and acetic acids which give the bio-oil its low pH. Although these are not strong acids, mild steel is attacked and storage should be in acid-proof materials such as stainless steel or polyolefins. Neutralisation causes rapid polymerisation of the polyphenols so the acidity has to be maintained unless the reactive compounds are managed in an alternative way, some of which are described later.

5.3. Density

The density of pyrolysis liquid is very high at around 1.2 kg/l. Thus, although the energy density is low in weight terms at around 17 MJU/kg at 25% water or 40% of the heating value of fossil derived fuel oil at around 42 MJ/kg, this corresponds to 20.5 MJ/l compared to about 33.5 MJ/l for fossil fuel oil i.e. 61% of the volumetric energy density.

5.4. HHV

The heating value of bio-oil is about 17 MJ/kg at 25% wt water which is about 40% that of fuel oil/diesel in weight terms. This means that 2.5 kg bio-oil is required for the same energy input as 1 kg fossil fuel oil, but only 1.5 l per litre of fossil fuel oil due to the high density.

5.5. Viscosity

The viscosity of crude bio-oil can vary over a wide range from as low as 10 cp at ambient temperature to as high as 10,000 cp or more from oil stored in poor conditions for long periods. The viscosity is a function of water content, process

configuration and process parameters, feedstock, storage conditions and age. There are currently no established relationships between any of these parameters, although viscosity or viscosity change is recognised as a major indicator of stability.

5.6. Solids

The primary method of char removal in a fast pyrolysis process is by a cyclone which becomes less effective as particle size reduces. Some char fines are therefore carried through the cyclone and collect in the bio-oil, typically resulting in a solids content of around 1%, although figures between 0.3–3% have been reported. This char could have deleterious effects on applications resulting in blockage, erosion, and high emissions from incomplete combustion, although most experience to date has not reported such problems.

The char can be removed in two main ways: hot vapour filtration and liquid filtration. Hot vapour filtration is analogous to hot gas cleaning in gasification processes and removes char after the cyclone and before liquids collection. This has been shown to be very effective giving a more translucent oil. The potential losses in oil yield from the increased vapour residence time and effect of catalytic cracking on the char layer on the filter as discussed above has been minimised in work carried out at NREL [143] and VTT. The alternative is to filter the liquid and cartridge filters, rotary pressure filters and centrifuges have been used with varying degrees of success. The pyrolytic lignin resulting from partial depolymerisation of lignin forms a gel-like consistency and rapidly blocks most conventional filter media.

An alternative strategy is to use the crude bio-oil and this has been successful with the development of a dual fuel diesel engine [144].

5.7. Stability

One of the key characteristics of bio-oil is its propensity to ‘age’ due to slow polymerisation or condensation type reactions with the polyphenols. This manifests as increasing viscosity and is accelerated by higher temperatures, exposure to oxygen and exposure to ultra-violet light. At temperatures above 100°C the effect results in phase separation.

The effect of feed, and process parameters on this instability is not fully understood, but is one of the important characteristics that require addressing to enable users to develop applications with confidence.

5.8. Quality

A key factor in the definition of liquid product quality is stability as discussed above and summarised in Table 29 together with the other characteristics described and many other features that are more specific to the application [145,146]. It is necessary to develop standards and specifications analogous to

those for conventional fuels so that suitable quality criteria can be developed for different applications [147].

An additional aspect is the use of traditional fuel characterisation test methods and their validity when applied to bio-oil [148]. Not all orthodox methods are valid and new methods may require to be developed or even invented. Key properties for use as a diesel substitute are viscosity, heating value, lubricity, density and stability.

6. Applications of liquid products

A very brief summary of the main applications for bio-oil is given here. The possibilities for the utilisation of crude and modified bio-oil are shown in Fig. 25 with un-proven steps shown in grey. Applications are described below and summarised in Table 30.

6.1. Combustion

Although the heating value of bio-oil is much lower than fossil fuel oil and it contains a significant proportion of water, it has been successfully used as a fuel by many organisations both in test campaigns and commercially. Tests have been successfully carried out at Canmet in Canada [149], at MIT, and by Neste in Finland [150], and the bio-oil is routinely used as a boiler fuel by Red Arrow in the USA. Problems reported are the high viscosity which is adjusted by addition

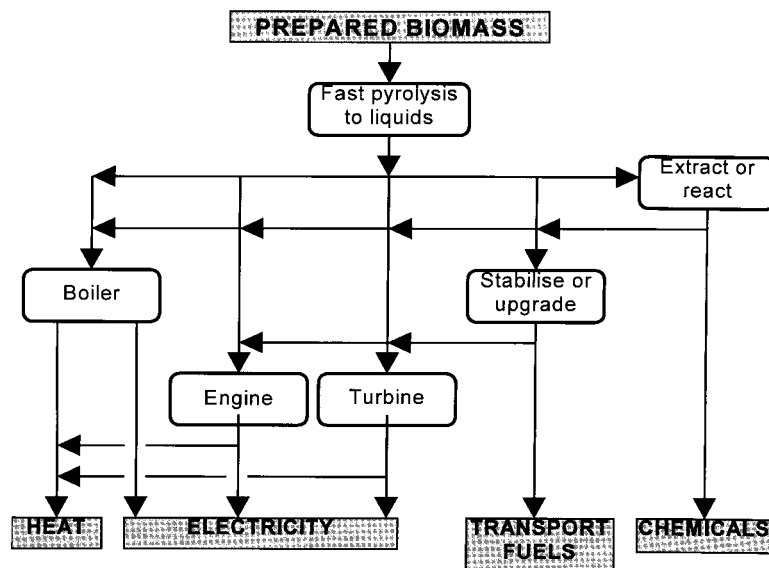


Fig. 25. Processes and products from fast pyrolysis of biomass.

Table 30
Summary of applications of pyrolysis liquid products

Combustion
<ul style="list-style-type: none"> • Once ignited, bio-oil burns readily, • Emissions are controllable, • <i>Minor equipment modifications and some handling precautions are needed</i>
Power generation with liquids
<ul style="list-style-type: none"> • Fuel production is de-coupled from power generation, • Dual fuel diesel engine successful at 250 kWe, • Turbine tests successful at 2.5 MWe, • <i>Uncertainty over stability and effects of ash & char,</i>
Liquid upgrading
<ul style="list-style-type: none"> • Hydrotreating to naphtha and diesel. Costly, requires hydrogen. Catalyst stability problems. • Zeolite cracking to aromatics. Less costly, no hydrogen, less efficient. Less developed. • <i>Costs too high for transport fuels.</i>
Liquid stabilisation
<ul style="list-style-type: none"> • Currently being investigated.
Chemicals
<ul style="list-style-type: none"> • Speciality chemicals • Intermediates e.g. polyphenols, fertilisers, environmental chemicals • <i>High value of chemicals may improve economics</i>

of alcohol by Neste [150] and by in-line preheating by Canmet [149]. In both cases, the boiler or furnace requires preheating with conventional fuels before switching over to bio-oil and a more complex start-up sequence is therefore required as bio-oil is not miscible with fuel oil or diesel. Once burning, emissions are quite acceptable.

6.2. Engines

Due to the higher added value of electricity compared to heat and its ease of distribution and marketing, electricity production has attracted considerable attention as an application, which has been encouraged by the various incentives on offer in different countries as described earlier. The results of extended engine tests are reported in these proceedings during which crude bio-oil without any pretreatment has been successfully burnt in a modified 250 kWe dual fuel diesel engine by Ormrod [144] who have acquired about 200 h of running experience. Other organisations who have also gained experience include Inst. Motori, Italy; Kansas University, USA; MIT, USA; Pasquali, Italy; and Wartsila, Finland. Long-term operational experience is required to establish optimum conditions and obtain sufficient data for warranties.

6.3. Gas turbines

Orenda have reported on the successful use of filtered bio-oil in a silo combustor fitted 2.5 MWe gas turbine [151], and ENEL have studied the effect of

bio-oil combustion in gas turbines in a static test rig. Long term operational experience is required to establish optimum conditions and obtain sufficient data for warranties.

6.4. Transport fuels and synthetic fossil fuels

Two routes to transport fuels are possible [152]—hydrotreating/hydrocracking to a naphtha-like product with upgrading to diesel [153,154]; or zeolite cracking to aromatics [155]. None of these routes is proven technically with most concern being over catalyst stability and life. In addition the high pressure and high hydrogen requirement of hydrotreating routes makes this route much too expensive. The zeolite route does not have these disadvantages, but still results in unacceptably high product costs.

6.5. Chemicals

The production of chemicals is potentially much more attractive due to their high value. A comprehensive review of opportunities has recently been published [156]. The only currently commercial application is for food flavourings such as liquid smoke but other possibilities include speciality chemicals for pharmaceuticals and synthons, fertilisers, environmental chemicals and resins. The current constraints inhibiting development is lack of defined markets and inadequately developed production methods. The co-production of chemicals and fuels undoubtedly offers the most interesting opportunities.

Fast pyrolysis of biomass for liquids production has been under research and development for nearly 20 years and has now achieved commercial status. In that time, a wide range of reactor configurations have been devised to achieve the basic process requirements that give high liquid yields. The significance of a liquid fuel with the possibilities of storage and/or transport to the user is now appreciated and gaining more widespread acceptance.

There is now only little room for improvement in the liquid yields being obtained of around 75–80% on dry wood feed. Improvement of oil quality is now considered more important either through better control of the pyrolysis reaction system including secondary reactions or through modification of the pyrolysis products either catalytically, physically or thermally. Other areas of potential improvement include pretreatment of feed to improve liquid quality and liquid collection systems.

There is demonstrably growing interest in utilising the pyrolysis liquids for energy and non-energy applications of which the latter have greater commercial interest from their potentially higher value. Integrated energy and chemical production plants are now recognised as having considerable potential for maximising economic viability of the process.

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